Russian Chemical Reviews **71** (6) 465 – 488 (2002) © 2002 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2002v071n06ABEH000719

Redox reactions of actinides in carbonate and alkaline solutions

V P Shilov, A B Yusov

Contents

I.	Introduction	465
II.	Redox potentials	465
III.	Reactions in carbonate solutions	465
IV.	Reactions in alkaline media	473
V.	Conclusion	486

Abstract. Data on redox reactions involving uranium, neptunium, plutonium and americium ions in carbonate and alkaline solutions are generalised. The results of kinetic studies of these reactions are analysed and their mechanisms are discussed. The bibliography includes 169 references.

I. Introduction

Progress in the chemistry of actinides has long been associated predominantly with the necessity of solving technological problems. Early chemical investigations were concerned primarily with the reactions of actinides in acidic media, whereas the reactions in alkaline media were little studied. However, these scarce data are of most interest. Thus, the use of carbonate and alkaline solutions made it possible to stabilise valence states of actinides, which are either unstable or difficult to prepare in acidic media. For instance, Am(IV) was stabilised and Cf(V) and Cm(VI) were first obtained in carbonate media. The most prominent example is the discovery of heptavalent neptunium, plutonium and americium, which gave impetus to the outburst of studies of alkaline solutions of actinides in the late 1960s and in the early 1970s. In recent years, interest in redox reactions of actinides in alkaline media was rekindled. The reason is that there is an acute need to solve a number of problems associated with storage and processing of alkaline waste of radiochemical industry, which were accumulated in large amounts at plants both in Russia and abroad. Extensive studies in this field gave new interesting results, which are not only of applied but also of scientific importance.

In the last decade, the properties of actinides in carbonate and alkaline media were surveyed in reviews. For example, the compositions and structures of carbonate complexes in solutions and in the solid state were covered in detail in the review;[1] however, no consideration was given to redox reactions. The report [2] was devoted to the chemistry of actinides in alkaline media, including redox reactions. Unfortunately, this report is not easily accessible to Russian researchers. Besides, the results of more recent investigations were published in the literature.

V P Shilov, A B Yusov Institute of Physical Chemistry, Russian Academy of Sciences, Leninsky prosp. 31, 119991 Moscow, Russian Federation. Fax (7-095) 952 53 08. Tel. (7-095) 330 41 70
E-mail: Shilov@ipc.rssi.ru (V P Shilov), Ioussov@ipc.rssi.ru (A B Yusov)

Received 20 March 2002
Uspekhi Khimii **71** (6) 533 – 558 (2002); translated by T N Safonova

The aim of the present review is to systematise and analyse the available data on redox reactions of uranium, neptunium, plutonium, americium and curium in bicarbonate, carbonate and alkaline solutions.† We do not consider the data on photochemical and radiochemical reactions, which were generalised in the publications [3, 4] in sufficient detail. Studies of electrochemical reactions involving actinide ions are also beyond the scope of our review.

II. Redox potentials

To predict the possibility of a particular redox reaction occurring, the data on redox potentials (hereinafter referred to as potentials) of actinide pairs in carbonate and alkaline media are required. The measured and estimated (calculated) formal potentials (*i.e.*, potentials at equal concentrations of the oxidised and reduced forms) are given in Table 1.

III. Reactions in carbonate solutions

It can be seen from Table 1 that tri- and tetravalent uranium, neptunium and plutonium can be oxidised by molecular oxygen, whereas trivalent neptunium and plutonium can also be oxidised by water (in the pH range of 9 – 12, the potentials of the O_2/H_2O and H_2O/H_2 pairs vary from 0.70 to 0.52 V and from -0.53 to -0.71 V, respectively).[38] Besides, U(V), Pu(V) and Am(IV) are unstable in disproportionation reactions, Np(VI) must oxidise Np(IV), whereas Am(VI) can oxidise Am(III) and Am(IV).

1. Disproportionation and reproportionation reactions

a. Disproportionation of actinides(V)

The kinetics of disproportionation of U(V) in carbonate solutions was examined by cyclic chronopotentiometry.[39] It was found that U(V), which was generated on the electrode surface through reduction of U(VI), rapidly disappeared in solution. This process is best described by a model on the basis of the second-order reaction

† It should be noted that the reaction mechanisms were not considered in most of original studies and it is impossible to make justified conclusions about these mechanisms based on the available data. In this connection, we write the reaction equations in the formal form, *i.e.*, denote actinide ions as Np(VI), Pu(IV), *etc*. In addition, many reactions proceed in rather broad ranges of pH or alkali concentrations due to which the valence state of the actinide ion may vary.

Table 1. Formal potentials of actinide pairs.

Solution	Potential of the pair /V (relative to the normal hydrogen electrode)				Ref.
	VII/VI	VI/V	V/IV	IV/III	
Uranium					
0.1 M $NaHCO_3$		−0.98 [a]	–	–	5
1 M $NaHCO_3$		−0.63 [b]	–	–	5
0.05 M Na_2CO_3		−0.671	–	–	6
0.75 M Na_2CO_3 + + 0.6 M $NaClO_4$		−0.527	–	–	7
0.1 – 3 M Na_2CO_3		−0.71	–	–	5
1 M K_2CO_3		−0.6	0	−2.08	8
1 M NaOH		−0.65	–	−2.6	9, 10
Neptunium					
0.05 M Na_2CO_3	–	0.445	–	–	6
1 M Na_2CO_3	–	0.44	–	–	11
2 M Na_2CO_3 (pH 13)	–	0.47 [b,c]	–	−1.4 [d]	12
2 M Na_2CO_3 (pH 13 – 14)	–	0.27 [b]	–	–	12
0.2 M K_2CO_3	–	0.43	–	–	13
0.8 M K_2CO_3	–	0.44	–	–	13
1 M K_2CO_3	–	0.44	0.1	−1.32	8
				−1.3 [b]	12
3 M K_2CO_3	–	0.44	–	–	13
1 M NaOH	0.582	0.18	–	–	14, 15
	0.587	0.12	0.13	−1.8	16, 17, 18, 19
4 M NaOH	0.462	–	–	–	20
10.4 M NaOH	0.225	–	–	–	20
1 M LiOH	0.604	–	–	–	21
2.5 M LiOH	–	0.1527	–	–	22
4 M LiOH	–	0.1498	–	–	22
Plutonium					
0.05 M Na_2CO_3	–	0.334	–	–	6
1 M Na_2CO_3	–	0.33	–	–	23
2 M Na_2CO_3	–	0.35 [c]	–	–	24
2 M Na_2CO_3 + + 1 M NaOH	–	0.33 [c]	–	–	24
2 M Na_2CO_3 + + 2 M NaOH	–	0.31 [c]	–	–	24
Plutonium					
1 M ($NaHCO_3$ + + Na_2CO_3) (pH 11.0)	–	–	0.3 – 0.35 [d]	–	
0.1 M K_2CO_3	–	0.30	–	–	13
1 M K_2CO_3	–	0.32	0.6	−0.495	8, 13
1 M NaOH	0.849	0.23	–	–	20, 25
	–	0.21	–	−0.95	26
4 M NaOH	–	–	0.44	–	25
		–	0.26 – 0.29	–	27
4.6 M NaOH	0.715	–	–	–	20
7.9 M NaOH	–	0.21	–	–	28
10.1 M NaOH	0.540	0.20	–	–	20, 28
2.5 M LiOH	–	0.2518	–	–	22
4 M LiOH	–	0.2556	–	–	22
Americium					
1 M Na_2CO_3	–	0.9	–	0.924	29, 30
2 M Na_2CO_3	–	–		0.887	30
2 M ($NaHCO_3$ + + Na_2CO_3) (pH 9.7)	–	–	–	0.92	31
2 M ($NaHCO_3$ + + Na_2CO_3) (pH 10)	–	0.975	–	0.89	30, 32, 33
		0.93	–	–	32
1 M K_2CO_3	–	0.90	0.5	0.86	8, 13
2.82 M ($KHCO_3$ + + K_2CO_3) (pH 8.87)	–	–	0.99		34
2.82 M ($KHCO_3$ + + K_2CO_3) (pH 11.2)	–	–	0.81		34
1 M NaOH	1.05	0.65	–	–	35, 36
		0.68	0.25 – 0.50	< 0.25	37
Curium					
1 M K_2CO_3	–	–	0.5	1.6	8
1 M NaOH	–	–	–	0.7	10

[a] Determined by polarography. [b] Determined by cyclic voltammetry scan. [c] The diffusion potential between a 2 M Na_2CO_3 solution and a saturated calomel electrode was ignored. [d] Estimated by us based on the data of the study;[24] under these conditions, an equilibrium mixture of Pu(VI), Pu(V) and Pu(IV) was formed.

$$-\frac{d[U(V)]}{dt} = 2k_d[U(V)]^2, \quad (1)$$

where k_d is the rate constant of disproportionation.

The rate constants for disproportionation of U(V) in a 1 M $NaHCO_3$ solution (pH 8.57, $T = 25$ °C) remains unchanged as the concentration of U(VI) is varied in the range from 1 to 10 mmol litre^{-1}. An increase in pH ‡ leads to a decrease in the constant k_d both at a constant CO_3^{2-} content (17 mmol litre^{-1}) and at a constant HCO_3^- content (0.68 mol litre^{-1}). In the pH range of 8.57 – 9.23, the constant k_d varies from ~15 – 20 to 2 – 3 litre mol^{-1} s^{-1}.

The following mechanism of the process was proposed:[39]

$$U(VI)O_2(CO_3)_3^{4-} + \bar{e} \longrightarrow U(V)O_2(CO_3)_3^{5-}, \quad (2)$$

$$U(V)O_2(CO_3)_3^{5-} + HCO_3^- \overset{K}{\rightleftharpoons} \rightleftharpoons U(V)O_2(HCO_3)(CO_3)^{2-} + 2\,CO_3^{2-}, \quad (3)$$

$$U(V)O_2(CO_3)_3^{5-} + U(V)O_2(HCO_3)(CO_3)^{2-} \xrightarrow{k_d} \longrightarrow U(VI)O_2(CO_3)_3^{4-} + U(IV)O_2(HCO_3)(CO_3)^{3-}, \quad (4)$$

$$U(IV)O_2(HCO_3)(CO_3)^{3-} \longrightarrow \text{stable form of U(IV)}.$$

The experimental $\log k_d - \log[HCO_3^-]$ plot yields a straight line with a slope of 0.84 ± 0.06. Consequently, the reaction order with respect to the bicarbonate ion is close to unity. The slope of the plot of k_d *vs.* the concentration of free carbonate ions (on the logarithmic coordinates) is equal to -1.87 ± 0.1, *i.e.*, is close to -2.

It should be emphasised that the reaction (2) proceeds on the electrode surface, whereas the reactions (3) and (4) take place in solution. In 0.25 – 1 M $NaHCO_3$ solutions, the solvated electron can lose the 'reducing' properties. Thus, it was found that Np(V) was oxidised to Np(VI) upon γ irradiation of its aerated or argon-

‡ In bicarbonate – carbonate solutions, pH is generally controlled by changing the ratio between $[CO_3^{2-}]$ and $[HCO_3^-]$.

saturated bicarbonate solutions. This oxidation did not take place in a solution of Na_2CO_3, whereas irradiation of Np(VI) led to its reduction.[40]

Disproportionation of Pu(V) was not examined. It was only noted that Pu(V), which was generated upon electrochemical reduction of Pu(VI) in a bicarbonate solution, underwent disproportionation with a high rate and exclusively Pu(IV) was accumulated in the solution.[23] An increase in pH slows down disproportionation of Pu(V) [like disproportionation of U(V)]. At pH 11.0, the process is completed in 6–8 h. The hexa-, penta- and tetravalent plutonium ions were found in the equilibrium mixture, *i.e.*, the following reaction took place

$$2\,\mathrm{Pu(V)} \rightleftharpoons \mathrm{Pu(VI)} + \mathrm{Pu(IV)}. \tag{5}$$

b. Disproportionation of Am(IV)

Americium(IV), which was prepared in bicarbonate-carbonate solutions by electrolytic oxidation of Am(III), was reduced with water (the first-order reaction with respect to americium) and underwent disproportionation (second-order reaction).[32, 33]

$$4\,\mathrm{Am(IV)} + 4\,H_2O \longrightarrow 4\,\mathrm{Am(III)} + O_2, \tag{6}$$

$$\mathrm{Am(IV)} + \mathrm{Am(IV)} \longrightarrow \mathrm{Am(III)} + \mathrm{Am(V)}. \tag{7}$$

In a 1.3 M $NaHCO_3$ + Na_2CO_3 solution (pH 10), the activation energy of the second-order reaction in the temperature range of 30–65 °C is 100.8 ± 4.0 kJ mol^{-1}.

In a 1.5 M $NaHCO_3$ + Na_2CO_3 solution, the rate constant for disproportionation of Am(IV) was measured at different pH by spectrophotometry.[41] Americium(IV) was prepared by irradiating a solution of Am(III) containing the BrO^- ions with UV light. After termination of irradiation, Am(IV) was transformed spontaneously into Am(III) and Am(V) according to the reactions (6) and (7) in a time varying from a few minutes to 3–4 days (depending on pH). The conversion of Am(IV) into Am(III) was 50%–65%.

Taking into account the final proportion of Am(III), it can be concluded that the second-order reaction (7) prevailed. The rate constant of this reaction increased from 6.6×10^{-2} to 262 litre mol^{-1} s^{-1} as pH was increased from 10.39 to 12.13.

In a 1.5 M $KHCO_3$ + K_2CO_3 solution, $2k_d$ increased from 6.6×10^{-2} to 450 litre mol^{-1} s^{-1} as pH was increased from 8.40 to 11.70.

Judging from the slopes of the plots of $2k_d$ *vs.* pH (on the logarithmic coordinates), the disproportionation reaction of Am(IV) in $KHCO_3$ + K_2CO_3 and $NaHCO_3$ + Na_2CO_3 solutions is second order with respect to the OH^- ions. This is attributable to the fact that the first step involves hydrolysis of americium carbonate complexes:

$$\mathrm{Am(CO_3)}_n\mathrm{(H_2O)}_m^{(2n-4)-} + \mathrm{OH}^- \rightleftharpoons \tag{8}$$
$$\rightleftharpoons \mathrm{Am(OH)(CO_3)}_n\mathrm{(H_2O)}_{m-1}^{(2n-3)-} + \mathrm{H_2O},$$

$$2\,\mathrm{Am(OH)(CO_3)}_n\mathrm{(H_2O)}_{m-1}^{(2n-3)-} \rightleftharpoons \tag{9}$$
$$\rightleftharpoons \mathrm{Am(H_2O)}_x\mathrm{(CO_3)}_3^{3-} + \mathrm{AmO_2(H_2O)}_y\mathrm{(CO_3)}_2^{3-} + z\,\mathrm{CO_3^{2-}}.$$

If the concentration of K_2CO_3 in a $KHCO_3$ + K_2CO_3 solution is higher than 3 mol litre^{-1}, disproportionation of Am(IV) proceeds much more slowly and this reaction is very slow at a concentration of 4.0–5.88 mol litre^{-1}. Apparently, this is associated with an increase in the number of the carbonate groups in the coordination sphere of Am(IV) resulting in a decrease in the potential of the Am(IV)/Am(III) pair and an increase in the potential of the Am(V)/Am(IV) pair. As a consequence, the equilibrium of the reaction (9) is sharply shifted to the left and Am(IV) becomes stable.

c. Reproportionation of Np(IV) + Np(VI)

The reaction

$$\mathrm{Np(IV)} + \mathrm{Np(VI)} \longrightarrow 2\,\mathrm{Np(V)} \tag{10}$$

was examined in 1.7–4.0 M K_2CO_3 solutions by spectrophotometry (λ = 490 nm).[42] The concentrations of Np(VI) and Np(IV) are lowered according to the equation

$$-\frac{\mathrm{d[Np(VI)]}}{\mathrm{d}t} = -\frac{\mathrm{d[Np(VI)]}}{\mathrm{d}t} = k'\mathrm{[Np(VI)][Np(IV)]}. \tag{11}$$

The apparent rate constant of the reaction k' remains virtually unchanged upon a twofold change in the concentrations of Np(VI) and Np(IV) and decreases by a factor of 4 as the K_2CO_3 content is increased from 1.71 to 4 mol litre^{-1}. The authors of the cited study [42] attributed this fact to an increase in the number of the carbonate groups in the complex Np(IV) ion [like in the Am(IV) ion, see above], which hinders charge transfer.

In the temperature range of 52–76.5 °C, the activation energy of the reaction (10) in K_2CO_3 solutions is 103 ± 2 kJ mol^{-1}, which is virtually equal to this value (104 kJ mol^{-1}) for the reproportionation reaction Np(IV) + Np(VI) in solutions of $HClO_4$ and HNO_3.

In the presence of sulfate ions, the reaction (10) slows down. The addition of SO_4^{2-} (0.21 mol litre^{-1}) to a 2.08 M K_2CO_3 solution led to a decrease in k' from 1470 to 390 litre mol^{-1} min^{-1}. Hence, the sulfate ion has a more substantial effect on the reaction rate than the carbonate ion. This fact remains to be explained.

2. Reactions analogous to disproportionation and reproportionation

a. Reactions of Am(III) with Am(VI)

Judging from the potentials of the Am(VI)/Am(V) and Am(IV)/Am(III) pairs in carbonate-bicarbonate solutions (see Table 1), Am(VI) can oxidise Am(III)

$$\mathrm{Am(III)} + \mathrm{Am(VI)} \overset{K}{\rightleftharpoons} \mathrm{Am(IV)} + \mathrm{Am(V)}. \tag{12}$$

Actually, Am(IV) and Am(V) are accumulated in solution when equimolar carbonate solutions containing tri- and hexavalent americium (6.2×10^{-4} M) are mixed in different proportions.[30] If the difference between the formal potentials is 60 mV ($[CO_3^{2-}]$ = 1 mol litre^{-1}), the rate constant

$$K = \frac{\mathrm{[Am(IV)][Am(V)]}}{\mathrm{[Am(III)][Am(VI)]}}$$

must be equal to 10 (the experimental value is 11.2 ± 1.5).

Hence, four valence forms, *viz.*, Am(III), Am(IV), Am(V) and Am(VI), can coexist in solutions with pH 9.5–10.5.

b. Reactions of Np(V) with Am(V)

The reaction

$$\mathrm{Np(V)} + \mathrm{Am(V)} \longrightarrow \mathrm{Np(VI)} + \mathrm{Am(III)}$$

was studied by spectrophotometry from the intensity of light absorption of Am(III) (λ = 508 nm) and Np(VI) (470 nm) in 0.45–1.71 M Na_2CO_3 solutions.[43] The Am(III) concentration was increased half as rapidly as the Np(VI) concentration. Hence, the following equation was proposed for this reaction:

$$2\,\mathrm{Np(V)} + \mathrm{Am(V)} = 2\,\mathrm{Np(VI)} + \mathrm{Am(III)}, \tag{13}$$

and a change in the concentrations of the reacting compounds is described by the equation

$$-\frac{\mathrm{d[Am(V)]}}{\mathrm{d}t} = -\frac{1}{2}\frac{\mathrm{d[Np(V)]}}{\mathrm{d}t} = k'\mathrm{[Am(V)][Np(V)]}. \tag{14}$$

The validity of the Eqn (14) is confirmed by the fact that the constant k' (T = 64 °C) is independent of the initial concentrations of Np(V) (0.65–1.9 mmol litre^{-1}) and Am(V) (0.65–1.3 mmol litre^{-1}). The reaction rate (the order with respect to the CO_3^{2-} ions $n = -1.53$) decreases monotonically as the Na_2CO_3 content is increased. In the temperature range of

50.5 – 69.7 °C, the activation energy is 60 ± 4 kJ mol^{-1} regardless of the Na_2CO_3 concentration.

Most likely, the process starts with dissociation of the Am(V) and Np(V) carbonate complexes [like in the case of disproportionation of U(V)]. Hence, we believe that at a constant ionic strength of solution (μ), the reaction order with respect to CO_3^{2-} would be more close to -2. In this medium, pentavalent actinides can exist as tricarbonate complexes.[1] In this case, it can be assumed that the following reactions proceed:

$$Am(V)O_2(CO_3)_3^{5-} \longrightarrow Am(V)O_2(CO_3)_2^{3-} + CO_3^{2-}, \quad (15)$$

$$Np(V)O_2(CO_3)_3^{5-} \longrightarrow Np(V)O_2(CO_3)_2^{3-} + CO_3^{2-}. \quad (16)$$

Next, the following charge transfer processes take place

$$Np(V)O_2(CO_3)_2^{3-} + Am(V)O_2(CO_3)_2^{3-} \rightleftharpoons Z, \quad (17)$$

$$Z \xrightarrow{\text{slow}} Np(VI)O_2(CO_3)_n^{x-} + Am(IV)(CO_3)_m^{y-}, \quad (18)$$

$$Np(V) + Am(IV) \xrightarrow{\text{fast}} Np(VI) + Am(III), \quad (19)$$

where Z is an activated complex.

c. Reactions of Am(III) with Np(VII)

In a 2.82 M $KHCO_3 + K_2CO_3$ solution, the potential of the Am(IV)/Am(III) pair varies from 0.99 to 0.81 V as pH is increased from 8.9 to 11.2.[34] In carbonate and bicarbonate media, the potentials of the Np(VII)/Np(VI) pair vary in the ranges which are apparently comparable with the range mentioned above or are even broader. Actually, the potential of this pair in a 1 M NaOH solution is 0.582 or 0.587 V (see Table 1) and increases by 0.118 V as pH is decreased by unity ($\mu = 1$),[16] *i.e.*, this potential at pH 11 and pH 10 must be no lower than 0.9 V and no higher than 1 V, respectively. In carbonate solutions, these values may vary due to the formation of the Np(VI) and Np(VII) complexes with the carbonate ions, but these changes are insignificant. Hence, Np(VII) can serve as an oxidiser of Am(III) in bicarbonate and carbonate media. However, Np(VII) is reduced with water under the same conditions. The yield of Am(IV) depends on the ratio between the reaction rates

$$Np(VII) + Am(III) \longrightarrow Np(VI) + Am(IV), \quad (20)$$

$$4\,Np(VII) + 2\,H_2O \longrightarrow 4\,Np(VI) + O_2. \quad (21)$$

After the addition of an aliquot of an alkaline solution of neptunium(VII) to a 1.5 M $KHCO_3$ solution of americium(III), the latter is oxidised already in the course of stirring (10 – 30 s).[44] The intensity of the absorption band of Am(III) carbonate complexes with a maximum at 507 nm decreases (in some cases, the band even disappears). The light absorption resulting from superposition of broad bands belonging to Am(IV) and Np(VI) is observed at wavelengths shorter than 450 nm. When the dry salt $K_4Fe(CN)_6 \cdot 3\,H_2O$ was placed in a cell, light absorption at 350 – 400 nm was decreased and the band with a maximum at ~507 nm simultaneously regained its initial intensity. This unambiguously indicates that Np(VII) oxidises Am(III) to Am(IV). The rate constant for the bimolecular reaction (20) is larger than 5×10^3 litre mol^{-1} s^{-1}.[44] This value is many orders of magnitude larger than the rate constant of the reaction (21) for which the conversion of Np(VII) at pH 9.08 reaches 50% in 1.2 min.[45] In the presence of a two- or threefold excess of Np(VII), Am(III) is also oxidised only to the tetravalent state.

The same phenomena are observed in $KHCO_3 + K_2CO_3$ or $NaHCO_3 + Na_2CO_3$ mixtures at pH $\leqslant$ 10.9. At higher pH (including 1.5 M K_2CO_3 or Na_2CO_3 solutions without additives of bicarbonate), the addition of a stoichiometric amount of Np(VII) leads to complete oxidation of Am(III) to Am(IV), which then disappears due to disproportionation [see the reaction (7)]. This is evidenced by the appearance of Am(III) in an amount half as large as the initial value. The reaction of Am(III) with Np(VII) taken in a threefold excess afforded Am(VI), which is characterised by light absorption at 450 – 600 nm. Hence, Np(VII) oxidises not only Am(III) but also Am(V)

$$Am(V) + Np(VII) \longrightarrow Am(VI) + Np(VI). \quad (22)$$

The addition of $K_4Fe(CN)_6 \cdot 3\,H_2O$ crystals to this solution led to a decrease in absorption at 450 – 600 nm but the absorption of Am(III) was not observed, *i.e.*, Am(VI) was reduced to Am(V).

The addition of a solution of Np(VII) in 0.01 M NaOH to a solution of Am(III) in 6 M K_2CO_3 resulted in oxidation of approximately one-half of the initial amount of Am(III). However, the absorption bands of Am(IV) and Am(VI) were not observed. The concentration of Am(III) was not increased upon the addition of $K_4Fe(CN)_6 \cdot 3\,H_2O$. Hence, Am(III) is partially oxidised to Am(V) in this medium

$$Am(III) + 2\,Np(VII) \longrightarrow Am(V) + 2\,Np(VI). \quad (23)$$

d. Reactions of Am(IV) with Np(IV) or Pu(IV)

In a 0.5 M $NaHCO_3$ + 1 M Na_2CO_3 solution, americium(IV) oxidises neptunium(IV), which is taken in an equimolar amount, to neptunium(VI) in 1 – 2 min.[46] The processes starts with the reaction

$$Am(IV) + Np(IV) \longrightarrow Am(III) + Np(V) \quad (24)$$

followed by the more rapid reaction (19), because only Am(III), Np(VI) and Np(IV) are present in the solution after the disappearance of Am(IV), *i.e.*, the process is described by the equation

$$Np(IV) + 2\,Am(IV) = Np(VI) + 2\,Am(III).$$

Compared to the reaction (24), oxidation of Pu(IV) with americium(IV)

$$Am(IV) + Pu(IV) \longrightarrow Am(III) + Pu(V) \quad (25)$$

proceeds more slowly.[47] The subsequent reaction

$$Am(IV) + Pu(V) \longrightarrow Am(III) + Pu(VI) \quad (26)$$

must proceed faster.

3. Oxidation reactions

a. Oxidation with molecular oxygen

Oxidation of uranium(V) in a 1 M Na_2CO_3 solution and oxidation of uranium(IV) in a 1 M $NaHCO_3$ solution with atmospheric oxygen were examined in the study.[5] In both cases, U(VI) was accumulated in the reaction products. The kinetic parameters of the reactions were not reported. The kinetics of U(IV) oxidation in carbonate-bicarbonate solutions was investigated.[48] When air was passed with a rate of 130 ml min^{-1} through a 1 M $NaHCO_3$ + 0.25 M Na_2CO_3 solution (40 ml) containing uranium (1.3×10^{-2} mol litre^{-1}), U(VI) was formed with a rate of 1.3×10^{-5} mol litre^{-1} min^{-1}. A threefold decrease in the concentration of $HCO_3^- + CO_3^{2-}$ led to an increase in the rate of oxidation by ~30%; the addition of copper ammoniate caused acceleration of oxidation.

Plutonium(III), which was prepared by electrolysis of Pu(IV) in a 1 M K_2CO_3 solution, underwent oxidation with atmospheric oxygen within a few minutes after termination of electrolysis. The supply of atmospheric oxygen was increased on stirring of the solution and oxidation was accelerated.[24]

Dissolution of NpO_2 crystals in an aerated 1 M $NaHCO_3$ solution was examined.[49] The rate of dissolution of NpO_2 in this solution (210 ppm per day) proved to be much higher than that in water (2.5 ppm per day) or in a saturated NaCl solution (25 ppm per day). Neptunium(V) was detected in bicarbonate solutions, which indicates that NpO_2 is oxidised under the action of O_2 and HCO_3^-.

b. Oxidation with hydrogen peroxide

Hydrogen peroxide was also used for uranium oxidation (a suspension of a UO_2 powder in 0.5 M $NaHCO_3$ or NH_4HCO_3

solutions, $T = 20\ ^{\circ}C$).[50] To accelerate dissolution of UO_2, $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ were added to the system. The proportion of uranium oxidised during the same period was approximately halved when pH was increased from 7.5 to 9, whereas a subsequent increase in pH has no effect on the oxidation rate.

c. Oxidation with water

Neptunium(III), which was prepared by an electrochemical method in a carbonate solution,[12] was spontaneously oxidised with water, which hindered the measurement of its absorption spectrum.

d. Oxidation with ozone

In the study,[51] solutions of Am(VI) and Am(V) were prepared with the use of ozone. When oxygen containing 5% O_3 was passed through a 0.1 M $NaHCO_3$ solution containing a suspension of $Am(OH)_3$ during 1 h, Am(VI) was formed quantitatively at any temperature in the range from 0 to 90 °C.

In a 2 M Na_2CO_3 solution, Am(III) is oxidised with ozone to Am(VI) at room and lower temperatures. In heated solutions, accumulation of Am(V) takes place.

Americium(V) involved in double carbonate with sodium was readily oxidised to Am(VI) with ozone in $NaHCO_3$ solutions at room temperature. However, ozone oxidised $Am(OH)_3$ in 0.03 – 0.1 M $KHCO_3$ solutions to form Am(V), which precipitated as the salt $KAmO_2CO_3$.

The kinetics of ozonation was not studied in detail. Nevertheless, some conclusions can be made about the mechanisms of the reactions that take place. Experiments on oxidation of Pu(III) with ozone in aqueous 0.25 – 1 M $HClO_4$ solutions enriched with the ^{18}O isotope demonstrated that water and ozone each supply one oxygen atom to form the PuO_2^{2+} ion.[52] Oxidation of U(IV) with ozone is also accompanied by the transfer of the oxygen atom from ozone (apparently, as an inner-sphere process).[53] Oxidation of Am(III) with ozone may be schematically described by the following equations (without considering the complex formation with the carbonate ions):

$$Am(III) + O_3 + 2\,OH^- \longrightarrow AmO_2^+ + O_2 + H_2O, \quad (27)$$

$$AmO_2^+ + O_3 \longrightarrow AmO_2^{2+} + O_3^{-\bullet}, \quad (28)$$

$$Am(III) + O_3^{-\bullet} \longrightarrow Am(IV) + O_2, \quad (29)$$

$$Am(IV) + O_3 + 2\,OH^- \longrightarrow AmO_2^{2+} + O_2 + H_2O. \quad (30)$$

In carbonate solutions, Am(III) exists as the complex $AmCO_3^+$, $Am(CO_3)_2^-$ or $Am(CO_3)_3^{3-}$ ions depending on the composition of these solutions.[54] Based on the two last-mentioned complex ions, the crystalline compounds $NaAm(CO_3)_2 \cdot 4\,H_2O$ and $Na_3Am(CO_3)_3 \cdot 3\,H_2O$ containing water molecules in the coordination sphere of Am(III) were obtained.[55] Oxidation with ozone is accompanied by the replacement of the water molecule in the coordination sphere of Am(III) followed by elimination of the oxygen molecule [see the reaction (27)]. This mechanism was confirmed by our experiments on oxidation of Am(III) with ozone in a 5 M K_2CO_3 solution. Apparently, an increase in the concentration of the carbonate ions leads to an increase in the number of the CO_3^{2-} groups in the coordination sphere of Am(III) due to the displacement of the water molecules as a result of which the insertion of the ozone molecule is hindered and oxidation occurs as an outer-sphere process to form Am(IV).

e. Oxidation with $S_2O_8^{2-}$ ions

Neptunium(V). The kinetics of Np(V) oxidation with the persulfate ions was studied by spectrophotometry from the change in absorption of Np(VI) at 470 nm.[56] A decrease in the concentration of Np(V) is described by the following equation

$$-\frac{d[Np(v)]}{dt} = 2\{k_1 + k_2[Np(V)]\}[S_2O_8^{2-}]. \quad (31)$$

It was found that two competitive reactions take place, *viz*., the first-order (rate constant k_1) and second-order (rate constant k_2) processes (the zero and first orders with respect to neptunium, respectively).

Variation in the $S_2O_8^{2-}$ concentration from 50 to 500 mmol litre^{-1} ([Np(V)] = 16 mmol litre^{-1} at 50 °C) has no effect on the rate constants k_1 and k_2 for Np(V) oxidation in a 0.94 M Na_2CO_3 solution. As the Na_2CO_3 concentration is increased from 0.84 to 1.92 mol litre^{-1} ($T = 50.4\ ^{\circ}C$), k_1 decreases from 4.7×10^{-5} to 2.3×10^{-5} min^{-1}, whereas the constant k_2 ($k_2 = 0.15$ litre mol^{-1} min^{-1}) remains unchanged.

In a 0.93 M K_2CO_3 solution, the constants k_1 and k_2 remain unchanged as $[Np(V)]_0$ is increased from 1.07 to 2.13 mmol litre^{-1} and $[S_2O_8^{2-}]_0$ is increased from 30 to 150 mmol litre^{-1}, but an increase in the K_2CO_3 concentration from 0.93 to 4.50 mol litre^{-1} ($T = 51.0\ ^{\circ}C$) is accompanied by a decrease in k_1 and an increase in k_2.

The activation energies of the first- and second-order reactions (E_1 and E_2, respectively) are 138 and 71 kJ mol^{-1}, respectively. The energy E_1 is virtually equal to the activation energy of thermal decomposition of $S_2O_8^{2-}$ (140 kJ mol^{-1}).[57] Hence, it can be assumed that the direct reaction of $S_2O_8^{2-}$ with Np(V) in carbonate solutions occurs simultaneously with thermal decomposition of $S_2O_8^{2-}$ followed by the reaction of the $SO_4^{-\bullet}$ radical ions with Np(V).

$$S_2O_8^{2-} \xrightarrow{k_1,\ slow} 2\,SO_4^{-\bullet}, \quad (32)$$

$$SO_4^{-\bullet} + CO_3^{2-} \xrightarrow{fast} SO_4^{2-} + CO_3^{-\bullet}, \quad (33)$$

$$Np(V) + CO_3^{-\bullet} \xrightarrow{fast} Np(VI) + CO_3^{2-}, \quad (34)$$

$$Np(V) + S_2O_8^{2-} \xrightarrow{k_2,\ slow} Np(VI) + SO_4^{-\bullet} + SO_4^{2-}. \quad (35)$$

Neptunium(IV). Oxidation of Np(IV) with persulfate ions was studied in 0.86 – 3.30 M K_2CO_3 solutions by spectrophotometry from a change in absorption of Np(VI) ($\lambda = 490$ nm) and Np(IV) ($\lambda = 800$ nm).[58] Typical kinetic curves for a decrease in the amount of Np(IV) and accumulation of Np(VI) assume an S shape. The concentration of Np(V) (calculated) passes through a maximum, which is reached within 10 – 15 min after the beginning of the reaction.

At constant temperature and concentration of K_2CO_3, the initial oxidation rate (V_0) of neptunium(IV) is independent of its initial concentration. The rate V_0 is comparable with the rate of thermal decomposition of the $S_2O_8^{2-}$ ions and is directly proportional to their concentration. Consequently, the process starts with the reactions (32) and (33) followed by the reaction

$$Np(IV) + CO_3^{-\bullet} \longrightarrow Np(V) + CO_3^{2-}. \quad (36)$$

The rate constant for this reaction was estimated at 6.9×10^3 litre mol^{-1} s^{-1}.[59] As Np(V) is accumulated, the contribution of the reactions (34) and (35) becomes more and more noticeable. Neptunium(VI) reacts with neptunium(IV) according to the reaction (10).

Neptunium(VI). In bicarbonate solutions containing Np(VI) (1.5 mmol litre^{-1}) and $S_2O_8^{2-}$ (50 mmol litre^{-1}), Np(VI) was only partially oxidised at 60 °C in the presence of alkali metal (potassium, sodium or lithium) or ammonium cations.[60] Accumulation of Np(VII) as $MNpO_4$ took place within first 30 min after mixing of the reagents, whereas subsequent storage of these reagents for 120 min led to only a slight increase in the Np(VII) content. As the concentration of $MHCO_3$ was increased from 16 to 46 mmol litre^{-1}, the yield of Np(VII) was increased from 17% to 44% in a $KHCO_3$ medium (pH 7.30 – 7.70) and from 18% to 29% in a $NaHCO_3$ medium (pH 7.30). A further increase in the $MHCO_3$ concentration led to a decrease in the yield of Np(VII). In aqueous solutions containing $KHCO_3$ (93 mmol litre^{-1}) or $NaHCO_3$ (46 mmol litre^{-1}), the formation of Np(VII) was not observed. In solutions of $LiHCO_3$ and NH_4HCO_3, the maximum yields of Np(VII) were lower.

The following scheme of the process can be proposed. Thermal decomposition of $S_2O_8^{2-}$ affords the $SO_4^{-\bullet}$ radical ions [see the reaction (32)]. Then, the following reactions proceed:

$$SO_4^{-\bullet} + H_2O \longrightarrow SO_4^{2-} + OH^{\bullet} + H^+, \quad (37)$$

$$HCO_3^- + SO_4^{-\bullet} \longrightarrow CO_3^{-\bullet} + SO_4^{2-} + H^+ \quad (38)$$

with the rate constants of 60 and 9.1×10^6 litre mol^{-1} s^{-1}, respectively.[61]

At a bicarbonate concentration of 10–100 mmol litre^{-1}, the $SO_4^{-\bullet}$ radical anions are predominantly consumed in the reaction (38). However, it is known that the $CO_3^{-\bullet}$ radical anion cannot oxidise Np(VI) in a carbonate medium.[62] Hence, either the $SO_4^{-\bullet}$ radical anion or the $S_2O_8^{2-}$ ion must serve as an oxidiser of Np(VI)

$$Np(VI) + SO_4^{-\bullet} \longrightarrow Np(VII) + SO_4^{2-}, \quad (39)$$

$$Np(VI) + S_2O_8^{2-} \longrightarrow Np(VII) + SO_4^{-\bullet} + SO_4^{2-}. \quad (40)$$

Neptunium(VII) is involved in two competitive processes. In one process, neptunium(VII) partially precipitates as the solid compound $MNpO_4$ (see Ref. 63) and is stabilised. In another process, the remaining Np(VII) is involved in a carbonate complex and reduced with water.[45]

Plutonium(IV). The kinetics of Pu(IV) oxidation with the $S_2O_8^{2-}$ ions in 1.07–1.57 M Na_2CO_3 solutions was studied by spectrophotometry from a change in light absorption of Pu(IV) and Pu(VI).[64] The initial oxidation rates of Pu(IV) to Pu(VI) linearly increased as the concentration of Pu(IV) was increased from 2 to 8 mmol litre^{-1} according to the empirical dependence

$$V_0 = a + b[Pu(IV)]. \quad (41)$$

It was assumed that two competitive processes of Pu(IV) oxidation occurred. The rate V_0 nonlinearly increased as the concentration of the $S_2O_8^{2-}$ ions was increased. Based on analysis of the experimental data, the following sequence of Pu(IV) oxidation with the $S_2O_8^{2-}$ ions was proposed. First, the reactions (32) and (33) proceed followed by the reactions

$$Pu(IV) + CO_3^{-\bullet} \longrightarrow Pu(V) + CO_3^{2-}, \quad (42)$$

$$Pu(V) + CO_3^{-\bullet} \longrightarrow Pu(VI) + CO_3^{2-}, \quad (43)$$

$$CO_3^{-\bullet} + CO_3^{-\bullet} \longrightarrow \text{products}. \quad (44)$$

Simultaneously, Pu(IV) reacts with the $S_2O_8^{2-}$ ions that remain undecomposed

$$Pu(IV) + S_2O_8^{2-} \longrightarrow \text{complex}, \quad (45)$$

$$\text{Complex} \longrightarrow Pu(V) + SO_4^{2-} + SO_4^{-\bullet}. \quad (46)$$

It was assumed [64] that Pu(IV) is oxidised directly with the $SO_4^{-\bullet}$ radicals. However, this reaction plays virtually no part in this medium. A change in the concentration of CO_3^{2-} has a substantial effect on the mechanism of the radical pathway of Pu(IV) oxidation and is only slightly reflected in intramolecular oxidation.

In the temperature range of 70–81.5 °C, the activation energies of radical and intramolecular oxidation are 134 ± 8 and 96 ± 8 kJ mol^{-1}, respectively.

Americium(III) and americium(V). Upon heating in a 0.1 M $NaHCO_3$ solution, americium(III) is oxidised under the action of $Na_2S_2O_8$ to Am(VI).[51] In a 2 M Na_2CO_3 solution in the presence of $Na_2S_2O_8$ (0.01 mol litre^{-1}), americium(VI) is formed only at 90 °C.[51] In a 0.1 M $KHCO_3 + K_2CO_3$ solution, americium(III) is oxidised under the action of the $S_2O_8^{2-}$ ions to americium(V), which precipitates as the $KAmO_2CO_3$ complex.

The kinetics of Am(III) oxidation with the persulfate ions was examined in solutions of K_2CO_3 (see Refs 65 and 66), $(NH_4)_2CO_3$ and Na_2CO_3 (see Ref. 66).§ The course of the reaction was followed from a change in light absorption of Am(III) (λ = 508 nm) and Am(VI) (λ = 688 nm [65] or 550 nm [66]). The concentration of Am(III) was decreased with a constant rate and this change slowed down only toward the end of the process. Accumulation of Am(VI) started when only 10% – 20% of Am(III) remained in the solution. Until then Am(VI), apparently, disappeared due to the involvement in the reaction (12) although the data on this process at high temperature are lacking. The higher was the CO_3^{2-} concentration and the lower was the $S_2O_8^{2-}$ concentration, the longer was the induction period. After completion of the induction period, Am(VI) was accumulated in solution almost linearly.

The rate of Am(III) oxidation is independent of the concentrations of americium (in the range of 0.25–1.58 mmol litre^{-1}) and K_2CO_3 and is directly proportional to the concentration of $S_2O_8^{2-}$ (12.5–200 mmol litre^{-1}).[65,66] At the same time, the rate of Am(V) oxidation, *i.e.*, the rate of Am(VI) accumulation, increases as the concentration of Am(V) is increased only to 0.6 mmol litre^{-1} and then remains constant. The formation of Am(VI) is accelerated as the concentration of $S_2O_8^{2-}$ is increased, whereas an increase in the K_2CO_3 content slows down the Am(VI) formation.

The activation energy of Am(III) oxidation is equal to that of Am(V) oxidation. These values are 143 ± 8 kJ mol^{-1} in a 1.9 M K_2CO_3 solution (T = 58–83 °C),[65] 143 ± 8 kJ mol^{-1} in a 1.5 M Na_2CO_3 solution and 159 ± 8 kJ mol^{-1} in a 1.9 M $(NH_4)_2CO_3$ solution.[66]

The following sequence of Am(III) and Am(V) oxidation can be proposed. Thermal decomposition of $S_2O_8^{2-}$ [see the reactions (32) and (33)] affords the $SO_4^{-\bullet}$ and $CO_3^{-\bullet}$ radical anions followed by the reactions

$$Am(III) + CO_3^{-\bullet} \longrightarrow Am(IV) + CO_3^{2-} \quad (47)$$

$$Am(V) + CO_3^- \longrightarrow Am(VI) + CO_3^{2-}, \quad (48)$$

and the reaction (12). The rate constant of the reaction (47) is 2.5×10^7 litre mol^{-1} s^{-1}.[67]

To our knowledge, americium(IV) does not react with $CO_3^{-\bullet}$ and, hence, Am(V) may be formed only upon disproportionation of Am(IV).

The plot of the rate constant for An(V) oxidation (An = U, Np or Pu) with the $CO_3^{-\bullet}$ radical anions *vs*. the potential of the An(VI)/An(V) pair yields a straight line on the logarithmic coordinates, which is characteristic of the Marcus outer-sphere electron transfer.[6] It is reasonable to suggest that oxidation of Am(V) will be described by an analogous plot. Extrapolation of the straight line to the potential of 0.92 V [*i.e.,* to Am(V)] gave $\log k \approx 6$ (litre mol^{-1} s^{-1}). This value is smaller than $\log k$ for the reaction (47) although the Am(VI)/Am(V) and Am(VI)/Am(III) pairs have similar potentials (see Table 1) and oxidation of both ions occurs without the structural rearrangements. Apparently, the lower rate of Am(V) oxidation as compared to the rate of Am(III) oxidation is responsible for the occurrence of the induction period observed upon accumulation of Am(VI). Taking into account that

$$k_{Am(III)}[Am(III)] \approx k_{Am(V)}[Am(V)],$$

for oxidation of Am(III) and Am(V) with persulfate ions we have

$$k_{Am(V)} \approx 0.1\, k_{Am(III)}.$$

The results obtained with the use of this ratio agree with the results of extrapolation. Our data on radiolysis and photolysis of Am(III) and Am(V) also indicate that these ions differ in their ability to be oxidised in carbonate solutions. Apparently, the $CO_3^{-\bullet}$ radical anions interact with Am(III) and Am(V) through different mechanisms. Oxidation of Am(V), like oxidation of U(V), Np(V) and Pu(V), proceeds through the outer-sphere charge transfer. By contrast, oxidation of Am(III) can be accompanied by hydrogen abstraction from the water molecule. It should be noted that oxidation of Am(III) with the $OH^{\bullet}$ radical in $HClO_4$ solutions proceeds through hydrogen abstraction from the water molecule involved in the hydration shell about the Am(III) ion.[68]

§ Semiquantitative data on the kinetics of this process published in earlier studies were surveyed in the review.[65]

A comparison of the calculated rates of formation of the $SO_4^{-\bullet}$ radical ions and oxidation of Am(III) shows that ~40% of the radical oxidisers goes into the latter reaction. The fact that Am(III) oxidation is somewhat accelerated in solutions containing more than 2 mol litre^{-1} of K_2CO_3 is indicative of the less significant role of side reactions rather than of the direct interaction of Am(III) with $S_2O_8^{2-}$ as has been suggested in the study.[66]

f. Oxidation with silver compounds

Americium(IV), which is unstable in acidic media, was stabilised in carbonate solutions. Americium(III) was subjected to the action of a mixture of $AgNO_3$ and $K_2S_2O_8$. In this case, several oxidisers appeared in the solution[69]

$$Ag(I) + S_2O_8^{2-} \longrightarrow Ag(II) + SO_4^{-\bullet} + SO_4^{2-}, \quad (49)$$

$$Ag(I) + S_2O_8^{2-} \longrightarrow Ag(III) + 2\,SO_4^{2-}, \quad (50)$$

$$Am(III) + Ag(II) \longrightarrow Am(IV) + Ag(I). \quad (51)$$

In addition, the reactions (33) and (47) took place.

Solid AgO also oxidises Am(III) to Am(IV).[69] Silver oxide was used also for oxidation of Pu(IV) in a 45% K_2CO_3 solution.[10,70] In the temperature range of 75–90 °C, complete oxidation of plutonium occurred during 45 min. Apparently, the following reactions proceeded:

$$Pu(IV) + Ag(I) \longrightarrow Pu(V) + Ag, \quad (52)$$

$$Pu(V) + Ag(I) \longrightarrow Pu(VI) + Ag, \quad (53)$$

along with the reaction (5).

g. Oxidation with ClO^- ions

It is known that macroamounts of Pu(IV) in a 45% K_2CO_3 solution are oxidised to Pu(VI) with the hypochlorite ions.[70] When heated to an above-room temperature, the reaction was completed in 5–10 min. The data on this process are scarce, which does not allow one to make conclusions about the reaction mechanism.

h. Oxidation with xenon compounds

The reactions of the americium ions with xenon compounds in bicarbonate and carbonate media were examined in the studies.[71–73] Xenon compounds were chosen as oxidisers in view of the fact that the potentials of the Xe(VIII)/Xe(VI) and Xe(II)/Xe(0) pairs are higher than the potentials of the Am(IV)/Am(III) and Am(VI)/Am(V) pairs. The calculated potential of the XeF_2/Xe pair in an acidic medium is 2.3 V.[74] In an alkaline medium, the potential of this pair was not determined but it was found that xenon difluoride partially oxidises Pu(VI) to Pu(VII) in 0.2–1.2 M NaOH solutions.[75] In a 1 M NaOH solution, the potential of the latter pair is 0.85 V. Hence, XeF_2 must oxidise Am(III).

The addition of a XeF_2 solution, which was cooled to 0 °C, to a 1.5 M $KHCO_3$ solution of Am(III) led to oxidation of the latter to Am(IV) in the course of stirring, which was established by spectrophotometry. The stoichiometric coefficient $n = \Delta[Am(IV)]/\Delta[XeF_2]$ is 0.23.[71,72] It should be noted that this is yet another known procedure for the chemical preparation of Am(IV) in carbonate solutions (photo- and electrochemical methods are not considered). Upon the addition of dry $K_4Fe(CN)_6 \cdot 3\,H_2O$ to the resulting solution, americium reverted to Am(III). In the presence of a tenfold excess of XeF_2, americium(III) was completely oxidised to Am(IV). Other valence states were not found. In a $KHCO_3 + K_2CO_3$ solution, the coefficient n decreased as the K_2CO_3 content was increased. In a 1.5 M K_2CO_3 solution, $n < 0.01$. In this medium, Am(III) was oxidised by at most 5%. In more concentrated K_2CO_3 solutions, americium(III) was not oxidised.

In aqueous solutions, not only does XeF_2 react with reducing agents but it also undergoes hydrolysis. The scheme of hydrolysis was proposed in the studies[76,77] and was thereafter substantiated.[78] Taking into account this scheme and the reactions of Am(III) and Am(IV), the following sequence of processes occurring in the course of Am(III) oxidation can be suggested. The reactions

$$XeF_2 + H_2O \longrightarrow XeO + 2\,HF, \quad (54)$$

$$XeO + H_2O \longrightarrow Xe + H_2O_2, \quad (55)$$

$$XeO + H_2O_2 \longrightarrow Xe + OH^{\bullet} + HO_2^{\bullet}, \quad (56)$$

$$HO_2^{\bullet} + OH^- \longrightarrow O_2^{-\bullet} + H_2O, \quad (57)$$

$$XeF_2 + O_2^{-\bullet} \longrightarrow XeF^{\bullet} + O_2 + F^-, \quad (58)$$

$$XeF^{\bullet} + OH^- \longrightarrow Xe + OH^{\bullet} + F^-, \quad (59)$$

$$OH^{\bullet} + HCO_3^- \longrightarrow CO_3^{-\bullet} + H_2O, \quad (60)$$

$$XeF^{\bullet} + HCO_3^- \longrightarrow Xe + F^- + HCO_3^{\bullet}, \quad (61)$$

are followed by the reaction (47) and then by the reactions

$$Am(IV) + HO_2^- \longrightarrow Am(III) + HO_2^{\bullet}, \quad (62)$$

$$Am(IV) + O_2^{-\bullet} \longrightarrow Am(III) + O_2. \quad (63)$$

The direct reactions of Am(III) with xenon compounds are also not ruled out.

$$Am(III) + XeF_2 \longrightarrow Am(IV) + XeF^{\bullet} + F^-, \quad (64)$$

$$Am(III) + XeF^{\bullet} \longrightarrow Am(IV) + Xe + F^-. \quad (65)$$

Oxidation of Am(III) under the action of Na_4XeO_6 in carbonate solutions was examined in the studies.[71,73] In an alkaline medium, the potential of the Xe(VIII)/Xe(VI) pair is close to 0.9 V.[79] This potential increases as pH is decreased and its values in a carbonate medium is higher than 1 V. Hence, the perxenate ion can oxidise americium(III) in bicarbonate and carbonate solutions. When $Na_4XeO_6 \cdot n\,H_2O$ was added to a 0.75 M $KHCO_3 + K_2CO_3$ solution (pH 10) containing Am(III) (2×10^{-4} mol litre^{-1}) until the concentration of the former reached 1×10^{-4} mol litre^{-1}, the mixture turned yellow already in 1 min. Analysis of the solution for different valence states of americium [by spectrophotometry and by reduction with $K_4Fe(CN)_6 \cdot 3\,H_2O$] revealed the presence of Am(IV), Am(V) and Am(VI). [Recall that XeF_2 oxidises Am(III) only to Am(IV)]. The $-\Delta[Am(III)]/\Delta[Xe(VIII)]$ ratio varied from 0.3 to 0.7. In the presence of a 30-fold excess of perxenate ions, americium was quantitatively oxidised to the hexavalent state. The same situation was observed in a 1.5 M $KHCO_3$ or K_2CO_3 solution. In a 5.9 M K_2CO_3 solution, perxenate ions decomposed and did not oxidise Am(III). As regards the mechanism of the reaction of Na_4XeO_6 with Am(III), the following conclusions can be made. If the process

$$CO_3^{2-} + Xe(VIII) \longrightarrow CO_3^{-\bullet} + Xe(VII) \quad (66)$$

took place, the subsequent reaction (47) would afford only Am(IV), which does not react with the $CO_3^{-\bullet}$ radical anions. For instance, this situation was observed upon photochemical oxidation of Am(III) in the presence of $S_2O_8^{2-}$, N_2O, BrO^- or BrO_3^- at pH 8.5–10.5.[41,80–82] The appearance of Am(V) and Am(VI) in solutions, where disproportionation of Am(IV) proceeds very slowly, indicates that Xe(VIII) serves as an oxidiser of americium to the pentavalent state

$$Am(III) + Xe(VIII) \longrightarrow Am(V) + Xe(VI), \quad (67)$$

$$Am(V) + Xe(VIII) \longrightarrow Am(VI) + Xe(VII), \quad (68)$$

$$Am(IV) + Xe(VIII) \longrightarrow Am(VI) + Xe(VI). \quad (69)$$

Two-electron reactions can proceed, for example, through the transfer of the oxygen atom. Americium(IV) involved in the reaction (69) is generated in the reaction (12). Like Xe(VIII), xenon(VII) can apparently oxidise Am(III), Am(IV) and Am(V). In addition, it was suggested that Xe(VII) is involved in the following processes:[83]

$$Xe(VII) + Xe(VIII) \longrightarrow Xe(VII)\cdot Xe(VIII), \quad (70)$$

$$Xe(VII)\cdot Xe(VIII) \longrightarrow Xe(VI) + Xe(IX), \quad (71)$$

$$2\,Xe(IX) \longrightarrow Xe(VIII) + Xe(VI) + O_2 \quad (72)$$

The rate constant of the reaction (72) is 2×10^7 litre mol^{-1} s^{-1}.

The reactions of Am(III) and Am(IV) with the perxenate ions can also proceed by a one-electron mechanism:

$$Am(III) + Xe(VIII) \longrightarrow Am(IV) + Xe(VII), \quad (73)$$

$$Am(IV) + Xe(VIII) \longrightarrow Am(V) + Xe(VII). \quad (74)$$

The ability of Na_4XeO_6 to oxidise Am(IV) was proved as follows. Trivalent americium (0.13 mmol litre^{-1}) in a 1.5 M $KHCO_3 + K_2CO_3$ solution was quantitatively oxidised to Am(IV) under the action of XeO_3 with the use of the photochemical method.[71] The addition of perxenate ions to the solution led to the rapid formation of Am(V) and Am(VI). The stoichiometric coefficient $-\Delta[Am(IV)]/\Delta[Xe(VIII)]$ was 0.2.

The potential of the XeO_3/Xe pair was estimated [84] at 2.10 and 1.24 V in acidic and alkaline solutions, respectively. Hence, XeO_3 could oxidise Am(III) in carbonate solutions. However, we experimentally established[71] that this reaction proceeded only under UV or γ irradiation.

i. β Decay as an oxidative process

Attempts to prepare curium(VI) by chemical methods failed due to the high oxidation potential of the Cm(IV)/Cm(III) pair and, presumably, low stability of curium(V). At the same time, there is reason to believe that Cm(VI) in carbonate solutions must be rather stable. Hence, another procedure for the preparation of Cm(VI) was chosen. This procedure makes use of β decay of the ^{242}Am isotope (half-life is 16.07 h). The compound $K_3AmO_2(CO_3)_2$, which was synthesised in the study,[85] contains americium with the following isotopic composition: 92% ^{241}Am, 1.4% ^{242}Am and 6.6% ^{243}Am. Before the synthesis, the starting americium specimen was purified from ^{242}Cm that was accumulated. The resulting compound was kept over a period from 18 to 40 h and then dissolved in a 0.1 M $NaHCO_3$ solution upon ozone bubbling to oxidise Am(V) to Am(VI). Under these conditions, curium(III) was not oxidised. It was expected that the daughter curium-242 isotope, which was generated *via* β decay of the ^{242}Am isotope in the course of storage of $K_3AmO_2(CO_3)_2$, would exist as the 'hot' ion, which has the parent composition but whose charge is larger by unity, *i.e.*,

$$AmO_2^+ \xrightarrow{\beta\ decay} CmO_2^{2+} + \bar{e}\,.$$

The estimation, which was carried out taking into consideration all nuclear-physics processes attendant on β decay of the ^{242}Am isotope, demonstrated that up to 60%–70% of the daughter ^{242}Cm isotope must be stabilised as the CmO_2^{2+} ions. The latter can be found after dissolution of $K_3AmO_2(CO_3)_2$. With the aim of establishing the valence state of ^{242}Cm, $K_4UO_2(CO_3)_3$ was precipitated from the resulting solution. The precipitate captured 96%–99% of AmO_2^+ and AmO_2^{2+} ions and only 3%–5% of Cm(III) ions. When the solution was in contact with freshly precipitated LaF_3, 97%–99% of the Cm(III) ions and no more than 3% of the Am(VI) ions were sorbed. Under the same conditions, 92%–95% of the NpO_2^+ ions (analogues of CmO_2^+) were sorbed. Experiments demonstrated that curium-242 was concentrated either with penta- and hexavalent actinides [in the $K_4UO_2(CO_3)_3$ precipitate] or only with hexavalent actinides (in a solution over the LaF_3 precipitate). Hence it follows that ^{242}Cm differs in chemical properties from curium(III), *i.e.*, ^{242}Cm was obtained in the hexavalent state.

This procedure was used also for the preparation of californium(V).[86] In carbonate solutions, the ^{249}Cf isotope, which is generated upon β decay of tetravalent berkelium-249, exists as Cf(V) sorbed on the $Na_4UO_2(CO_3)_3$ precipitate.

4. Reduction reactions

a. Reduction with water

Neptunium(VII). The gradual transformation of Np(VII) into Np(VI) in carbonate solutions was studied by spectrophotometry from a change in the intensity of absorption at $\lambda = 460$ nm.[45] For a 0.5 M $KHCO_3 + K_2CO_3$ solution with $\mu = 1$, the change in the Np(VII) concentration is described by the equation

$$-\frac{d[Np(VII)]}{dt} = k[Np(VII)]. \quad (75)$$

At 25 °C, the constant k decreases from 56.4×10^{-2} to 0.79×10^{-2} min^{-1} as pH is increased from 9.08 to 11.03. The plot of log k *vs.* pH yields a straight line with a slope of -0.98, *i.e.*, this reaction is first order with respect to the hydrogen ions (or reciprocal first order with respect to the OH^- ions). In the temperature range of 25–35 °C, the activation energy of reduction of Np(VII) to Np(VI) was estimated [45] at 33 kJ mol^{-1} (pH 10.0).

Instability of Np(VII) in carbonate solutions results from the high oxidation potential of the Np(VII)/Np(VI) pair ($\geqslant 1$ V; see Section III.2.c). Under these conditions, the potential of oxygen liberation from water is 0.64 V.

It is commonly assumed that the first step of H_2O decomposition under the action of strong oxidisers involves hydrogen abstraction to form the $OH^\bullet$ radical. However, the oxidation potential of the $OH^\bullet/OH^-$ pair at pH 10 is 2.1 V. Due to the large difference in the potentials of the above pairs, reduction of Np(VII) with water cannot proceed through the formation of the $OH^\bullet$ radical. However, another reaction, *viz.*, oxidation of water to H_2O_2 is also thermodynamically possible. The standard potential of the H_2O_2/H_2O pair is 1.77 V. In carbonate solutions, this potential is lowered to 1.1–1.2 V. For the reaction to follow this pathway, two Np(VII) ions must be simultaneously involved in this reaction. However, this reaction is first order with respect to neptunium. To resolve this contradiction, it was suggested [87,88] that the thermally excited Np(VII) ion and the nonexcited Np(VII) ion form a dimer through two OH groups. This dimer subsequently decomposes into two Np(VI) ions and the H_2O_2 water molecule. Hydrogen peroxide reduces two more Np(VII) ions.

Americium(VI) and americium(IV). The overall equation for reduction of Am(VI) with water in a 1.3 M Na_2CO_3 solution (pH 11.25) has the form

$$4\,Am(VI) + 4\,OH^- = 4\,Am(V) + O_2 + 2\,H_2O \quad (76)$$

(taking into account the high pH of the medium, the hydroxy ions rather than water molecules formally serve as a reducing agent).

At 25 °C, the rate constant for the first-order reaction was estimated at $(0.14 \pm 0.01) \times 10^{-4}$ s^{-1}. In the temperature range of 25–75 °C, the activation energy is 63.8 ± 4 kJ mol^{-1} (see Refs 32 and 33).

In a 1.3 M $NaHCO_3 + Na_2CO_3$ solution (pH 10), the rate constant (at 30 °C) for reduction of Am(IV) with water [see the reaction (6)] is $(0.6 \pm 0.3) \times 10^{-4}$ s^{-1}. In the temperature range of 30–65 °C, the activation energy is 96.6 ± 12.0 kJ mol^{-1} (see Ref. 33).

Probably, the mechanisms of Am(VI) and Am(IV) reduction with water are analogous to the mechanism of Np(VII) reduction.

b. Reduction with hydrogen peroxide

Plutonium(VI). The reaction of Pu(VI) with H_2O_2 was studied in 0.005–0.1 M $NaHCO_3$ solutions by stopped-flow spectrophotometry.[89] The results of this study indicate that the following reaction takes place

$$2\,Pu(VI) + H_2O_2 + 2\,OH^- \longrightarrow 2\,Pu(V) + O_2 + 2\,H_2O. \quad (77)$$

It was established experimentally that Pu(VI) forms a complex with H_2O_2. Thus, a 0.05 M $NaHCO_3$ solution containing Pu(VI) (0.6 mmol litre^{-1}) was injected into a 0.05 M $NaHCO_3$ solution containing H_2O_2 (3 mmol litre^{-1}). The rate constant for the formation of the Pu(VI) complex with H_2O_2 (k) was estimated at

$(6.9 \pm 0.8) \times 10^3$ litre mol^{-1} s^{-1}. Doubling of the initial H_2O_2 concentration led to an increase in the constant k to $(7.2 \pm 0.7) \times 10^3$ litre mol^{-1} s^{-1}. The rate of disappearance of the complex cannot be described by the first-order equation. Reduction began with the reactions [89]

$$\text{Pu(VI)} + H_2O_2 \longrightarrow \text{complex}, \quad (78)$$

$$\text{Complex} \longrightarrow \text{Pu(V)} + HO_2^{\bullet}. \quad (79)$$

According to the scheme proposed in the study,[89] the subsequent step involves the reaction of Pu(VI) with $HO_2^{\bullet}$ followed by other reactions. However, rather high pH was not taken into account. Since the reaction (57) is efficient at pH 8.5, it is apparently followed by the processes

$$\text{Pu(VI)} + O_2^{-\bullet} \longrightarrow \text{Pu(V)} + O_2, \quad (80)$$

$$O_2^{-\bullet} + H_2O_2 \longrightarrow OH^{\bullet} + OH^- + O_2, \quad (81)$$

and then by the reactions (60) and (43).

When Pu(VI) and H_2O_2 were taken at the initial concentrations of 0.11 and 11.2 mmol litre^{-1}, respectively, the apparent rate constant of the first-order reaction [see Eqn (79)] increased from 1.12 to 24.2 s^{-1} as the concentration of HCO_3^- was decreased from 0.05 to 0.005 mol litre^{-1}. An increase in the concentration of H_2O_2 in a 0.005 M $NaHCO_3$ solution from 11 to 22 mmol litre^{-1} led to an increase in the first-order rate constant from 24 to 34 s^{-1}.

c. Reduction with $Fe(CN)_6^{4-}$ ions

Neptunium(VI). Reduction of Np(VI) with the $Fe(CN)_6^{4-}$ ions was studied in aqueous solutions of Na_2CO_3 ($[Na_2CO_3] \leqslant 0.05$ mmol litre^{-1}) by the stopped-flow method.[90] For the process in a 0.05 M Na_2CO_3 solution,

$$\frac{\Delta[\text{Np(VI)}]}{\Delta[Fe(CN)_6^{4-}]} = 1.01 \pm 0.01,$$

which corresponds to the reaction

$$\text{Np(VI)} + Fe(CN)_6^{4-} \rightleftharpoons \text{Np(V)} + Fe(CN)_6^{3-}. \quad (82)$$

The kinetics of the reaction is described by the empirical equation

$$-\frac{d[\text{Np(VI)}]}{dt} = k'[\text{Np(VI)}][Fe(CN)_6^{4-}], \quad (83)$$

where $k' = (a + b[CO_3^{2-}])^{-1}$.

In a 0.004 M Na_2CO_3 solution (μ was maintained at 0.2 by adding NaCl) $k' = 2.8 \times 10^3$ litre mol^{-1} s^{-1} (at 25 °C). At a constant concentration of Na_2CO_3 (0.004 mol litre^{-1}), the change in the ionic strength from 0.1 to 1 had no effect on k' but the same increase in μ in a 0.05 M Na_2CO_3 solution led to doubling of k'.

The mechanism of reduction involves the following reactions:

$$NpO_2(CO_3)_3^{4-} + Fe(CN)_6^{4-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + CO_3^{2-}, \quad (84)$$

$$A \xrightarrow{k_2} \text{products}, \quad (85)$$

where A is an intermediate formed upon the replacement of one CO_3^{2-} group in $NpO_2(CO_3)_3^{4-}$ by the $Fe(CN)_6^{4-}$ ion.

Plutonium(VI). The reaction of Pu(VI) with the $Fe(CN)_6^{4-}$ ions proceeds [91] analogously to the reaction of Np(VI) with these ions considered above

$$\text{Pu(VI)} + Fe(CN)_6^{4-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{Pu(V)} + Fe(CN)_6^{3-}. \quad (86)$$

In a 0.05 M Na_2CO_3 solution (25 °C), $k_f = 1214 \pm 20$ and $k_r = (3.64 \pm 0.20) \times 10^4$ litre mol^{-1} s^{-1} for the forward (f) and reverse (r) reactions, respectively. The empirical dependence of the rate constant for the forward reaction on the concentration of the carbonate ions takes the form

$$\ln k_f = \ln a + n \ln[CO_3^{2-}]. \quad (87)$$

At 25 °C, $\ln a = 4.74 \pm 0.11$ and $n = 0.80 \pm 0.03$ for $\mu = 0.2$ (NaCl), [Pu(VI)] = 0.2 mmol litre^{-1}, $[Fe(CN)_6]^{4-} = 0.4$ mmol litre^{-1}. The rate constant k_r is virtually independent of the CO_3^{2-} concentration.

The reactions (82) and (86) have much in common. However, it is not improbable [91] that these reactions proceed through different mechanisms. In particular, the characteristics of the reaction (82) are inconsistent with the mechanism of the outer-sphere electron transfer, which seemed to be most probable.

Americium(IV) and americium(VI). The reactions of Am(IV) and Am(VI) with the $Fe(CN)_6^{4-}$ ions were not studied in detail. Nevertheless, it is known that these reactions in bicarbonate-carbonate media afford Am(III) and Am(V), respectively. Americium(V) is resistant to the hexacyanoferrate(II) ions. As mentioned above, the ratio between Am(IV) and Am(VI) in the initial mixture can be precisely established with the use of reduction with the $Fe(CN)_6^{4-}$ ions followed by the determination of the reaction products by spectrophotometry.

d. Reduction with the $[Tc(DMPE)_3]SO_3CF_3$ and $[Re(DMPE)_3]SO_3CF_3$ compounds

The $[M(DMPE)_3]SO_3CF_3$ compounds [M = Tc, Re, DMPE is 1,2-bis(dimethylphosphino)ethane] serve as outer-sphere reducing agents. These compounds were used in studies of the reactions with Np(VI) and Pu(VI) in carbonate solutions.[92] The equilibrium constants of the reactions

$$[An(VI)O_2(CO_3)_3]^{4-} + [M(I)(DMPE)_3]^+ \rightleftharpoons$$
$$\rightleftharpoons [An(V)O_2(CO_3)_3]^{5-} + [M(II)(DMPE)_3]^{2+}$$

($T = 25$ °C, $\mu = 0.3$, $[CO_3^{2-}] = 0.05$ mol litre^{-1}) were calculated. The rate constants and the activation energies of these reactions were determined. The rate constants of the self-exchange reactions for the Np(VI)/Np(V) and Pu(VI)/Pu(V) pairs, which were calculated according to the Marcus equation, are 0.69 and 3.0 litre mol^{-1} s^{-1}, respectively, when $Tc(DMPE)_3^+$ was used as a reducing agent and are 0.64 and 8.9 litre mol^{-1} s^{-1}, respectively, when $Re(DMPE)_3^+$ was used as a reducing agent.

IV. Reactions in alkaline media

1. Disproportionation and reproportionation reactions

a. Disproportionation of Np(VI) and Am(VI)

The necessary condition for self-oxidation–self-reduction reactions of hexavalent actinides is the similarity of the formal potentials E_f for the VII/VI and VI/V pairs. In the case of neptunium and americium, the potentials of these pairs in 1 M NaOH solutions differ by ~0.4 V. An increase in the alkali concentration leads to a sharp decrease in the potentials $E_f^{VII/VI}$, whereas $E_f^{VI/V}$ are changed only slightly. Hence, penta-, hexa- and heptavalent neptunium or americium can coexist in 10 M and more concentrated NaOH solutions.

Upon rapid 10–20-fold dilution with a 17 M NaOH solution, a colourless 5×10^{-3} M neptunium(VI) solution turned green, which is characteristic of Np(VII).[93] The visible regions of the absorption spectra of these solutions, which were measured after the removal of a suspension of air bubbles, were similar to the absorption spectrum of Np(VII). The difference was observed only in the short-wavelength region [due to the presence of Np(VI) in the solution]. The equilibrium

$$2\,\text{Np(VI)} \rightleftharpoons \text{Np(VII)} + \text{Np(V)} \quad (88)$$

was established at room temperature in less than 1 min. The position of the equilibrium depends substantially on the NaOH concentration. The determined equilibrium constants

$$K = \frac{[\text{Np(VII)}][\text{Np(V)}]}{[\text{Np(VI)}]^2}$$

in solutions with different compositions are given in Table 2.

Disproportionation of Np(VI) was studied also in hot NaOH solutions.[94] Under these conditions, the solubilities of neptunates are much higher as compared to those in the cold. In addition, the viscocity of alkaline solutions decreases as the temperature is increased due to which the formation of a suspension of air bubbles ceases. The determined equilibrium constants are well reproducible.

Table 2. Equilibrium concentrations of Np(VII) and equilibrium constants K for disproportionation reactions of Np(VI) in alkaline solutions ($T = 21-23$ °C).[93]

[NaOH] /mol litre^{-1}	10^4 [Np(VI)]$_0$ /mol litre^{-1}	10^4 [Np(V)] /mol litre^{-1}	10^5 [Np(VII)]$_p$ /mol litre^{-1}	10^2 K
8.7	9.52	–	1.2	0.017
10.7	9.52	–	3.5	0.16
11.8	2.38	–	1.4	0.44
12.4	5.00	–	3.8	0.8
13.6	2.38	–	2.8	2.4
14.8	4.55	–	7.8	6.8
15.3	2.38	–	4.3	8.0
17.2	2.38	–	5.1	13.2
13.6	2.38	0.33	1.8	2.2
13.6	2.38	0.84	1.5	3.4
13.6	2.38	2.50	0.45	2.5

Interestingly, the equilibrium constants are virtually independent of the temperature under the conditions studied. Consequently, the activation energies of Np(VI) disproportionation and Np(VII) reduction with pentavalent neptunium must be equal within the experimental error.

When studying disproportionation of actinides in aqueous solutions of KOH and CsOH and in aqueous-methanolic solutions of KOH, Tananaev[95] found that the nature of alkali is of little importance, whereas a decrease in the water content is favourable for disproportionation. For example, disproportionation in a solution containing 60 vol.% of methanol proceeds to a noticeable extend even at [KOH] = 4 mol litre^{-1}.

Disproportionation of Am(VI) was examined in the study.[96] A 18 M NaOH solution (2.5–3.0 ml) cooled to 0 °C and a cooled weakly acidic 0.03 M americium(VI) solution (0.2 ml) were mixed in a quartz cell and the absorption spectrum of the mixture was recorded. This spectrum had a band with a maximum at 740–750 nm, which is characteristic of Am(VII). Since there were no other oxidisers in the solution, the formation of Am(VII) was attributed to self-oxidation–self-reduction of Am(VI)

$$2\,\text{Am(VI)} \rightleftharpoons \text{Am(VII)} + \text{Am(V)}. \tag{89}$$

Table 3. Equilibrium constants for disproportionation reaction of Am(VI) in NaOH solutions at 0–3 °C.

[NaOH] /mol litre^{-1}	10^3 [Am(VI)]$_0$ /mol litre^{-1}	Equilibrium concentration /mol litre^{-1}			K
		Am(VII)	Am(V)	Am(VI)	
8.5	1.74	not found	–	–	–
12.4	1.61	0.20	0.20	1.21	2.7×10^{-2}
14.2	2.04	0.34	0.34	1.36	6.2×10^{-2}
15.4	2.30	0.80	0.80	0.70	1.3
16.6	1.37	0.45	0.45	0.47	0.9
17.2	1.39	0.61	0.61	0.17	13

The estimated equilibrium constants of this reaction are given in Table 3.

Americium(VI) is somewhat more prone to disproportionation than neptunium(VI). In both cases, the NaOH concentration has a similar effect on the equilibrium of the reaction.

b. Disproportionation of Pu(V)

Comparison of the potentials of the Pu(V)/Pu(IV) and Pu(VI)/Pu(V) pairs shows that Pu(V) must undergo disproportionation in a wide range of alkali concentrations. The kinetics of this process was studied by spectrophotometry.[97] In experiments, Pu(V) was prepared predominantly by reducing Pu(VI) with H_2O_2 in an alkaline medium

$$\begin{aligned} &H_2O_2 + OH^- \longrightarrow HO_2^- + H_2O, \\ &2\,PuO_2(OH)_4^{2-} + HO_2^- \longrightarrow \\ &\longrightarrow 2\,PuO_2(OH)_3^{2-} + O_2 + OH^- + H_2O. \end{aligned} \tag{90}$$

Then the accumulation of Pu(VI) in the solution was tracked. When precipitating, plutonium(IV) captured a portion of Pu(V). Taking into account the balance of all valence states of plutonium in the solution and in the precipitate [without considering reduction of Pu(VI) with α-radiolysis products of water], it was concluded that the following reaction proceeds in the solution:

$$2\,\text{Pu(V)} \rightleftharpoons \text{Pu(VI)} + \text{Pu(IV)}. \tag{5}$$

In alkaline media, Pu(V) exists as the $PuO_2(OH)_3(H_2O)^{2-}$ and $PuO_2(OH)_4^{3-}$ ions, freshly precipitated Pu(IV) exists as $Pu(OH)_4$ (more precisely, as $PuO_2\cdot n\,H_2O$) and Pu(VI) occurs as $PuO_2(OH)_4^{2-}$ (see Ref. 2). Hence, the reaction (5) can be described as follows:

$$\begin{aligned} &2\,PuO_2(OH)_3(H_2O)^{2-} \rightleftharpoons \\ &\rightleftharpoons PuO_2(OH)_4^{2-} + PuO_2\cdot n\,H_2O + m\,OH^-. \end{aligned} \tag{91}$$

The constant $2k$ was estimated from the initial rate of disproportionation of Pu(V)

$$V_0 = -\frac{\mathrm{d}[\text{Pu(v)}]}{\mathrm{d}t} = 2k[\text{Pu(v)}]^2. \tag{92}$$

It was found that the rate constant sharply increased as the NaOH concentration was decreased from 7.6 to 0.5 mol litre^{-1}. On the logarithmic coordinates, the plot of $2k$ *vs.* the activity of the OH^- ions yields a straight line with a slope of -2.8. However, taking into account that the activity coefficient of Pu(V) decreases on going from a 0.5 M NaOH solution to a 7.6 M solution, it can be assumed that the reaction order with respect to the OH^- ions is close to -2. Consequently, the fast step preceding the formation of an activated complex, proceeds with the replacement of the OH group in the Pu(V)-containing $PuO_2(OH)_3(H_2O)^{2-}$ ion by the H_2O molecule

$$PuO_2(OH)_3(H_2O)^{2-} + H_2O \rightleftharpoons PuO_2(OH)_2(H_2O)_2^- + OH^-, \tag{93}$$

i.e., as expected, lower-charged species are involved in the reaction.

The constant $2k$ increases as the temperature is increased. Thus, an increase in the temperature of a 3.3 M NaOH solution from 10 to 30 °C leads to an increase in $2k$ from 0.51×10^{-2} to 6.15×10^{-2} litre mol^{-1} s^{-1}. The activation energy is approximately 88 kJ mol^{-1}.

The results of experiments with Np(V) in 0.5–1 M LiOH, NaOH, KOH and CsOH solutions at 25–80 °C demonstrated that Np(V) remained unchanged in the conditions under study.

c. Reproportionation Np(VII) + Np(V) and Pu(VII) + Pu(V)

As mentioned above, the potential of the Np(VII)/Np(VI) pair sharply increases at the alkali concentration of $\leqslant 10$ mol litre^{-1} and the reaction (88) goes in the reverse direction

$$Np(VII) + Np(V) \rightleftharpoons 2\,Np(VI). \quad (94)$$

An analogous reaction proceeded also with plutonium

$$Pu(VII) + Pu(V) \rightleftharpoons 2\,Pu(VI), \quad (95)$$

because the potential of the Pu(VII)/Pu(VI) pair is substantially higher than the potential of the Pu(VI)/Pu(V) pair in a wide range of alkali concentrations. The kinetics of the reaction (94) in a LiOH solution was studied by pulse radiolysis.[98] It was established that the rate constant of the reaction is independent of the alkali concentration in the range of 0.033–2.0 mol litre^{-1} and its average value in a LiOH solution is $(2.3 \pm 0.9) \times 10^7$ litre mol^{-1} s^{-1}. In NaOH solutions, the rate constants of the reaction are smaller. Apparently, the reaction (95) also proceeds with a high rate.

d. Reproportionation Np(VI) + Np(IV) and Pu(VI) + Pu(IV)
The reaction

$$Np(IV) + Np(VI) \rightleftharpoons 2\,Np(V) \quad (10)$$

in deaerated 0.025–4.0 M LiOH solutions was examined in the study.[18] The reaction was completed in the course of stirring of a suspension of Np(IV) hydroxide in a LiOH solution with a Np(VI) solution in the same alkali. The formal potential of the Np(V)/Np(IV) pair was estimated from the equilibrium constants.

The addition of an equimolar amount of Pu(VI) to a 4 M NaOH solution containing Pu(IV) hydroxide led to the rapid formation of Pu(V),[25] *i.e.*, the following reaction proceeded:

$$Pu(VI) + Pu(IV) \rightleftharpoons 2\,Pu(V). \quad (96)$$

2. Reactions analogous to disproportionation and reproportionation

a. Reactions of Np(VI) with Pu(VII) and Pu(VI)
The reaction

$$Np(VI) + Pu(VII) \longrightarrow Np(VII) + Pu(VI) \quad (97)$$

proceeds rapidly at room temperature.[99] This reaction is irreversible at any concentrations of alkali because Pu(VII) is a stronger oxidiser than Np(VII) and the potentials of the Pu(VII)/Pu(VI) and Np(VII)/Np(VI) pairs change in parallel with the OH^- concentration.

In alkaline solutions, Np(VI) can be oxidised not only with heptavalent but also with hexavalent plutonium.[28] The reaction

$$Np(VI) + Pu(VI) \rightleftharpoons Np(VII) + Pu(V) \quad (98)$$

is reversible and proceeds with a high rate, which indicates that the ions of penta-, hexa- and heptavalent actinides in concentrated alkaline solutions have similar structures. According to the recent EXAFS study,[100] neptunium(VII) in alkaline solutions is involved in the $NpO_4(OH)_2^{3-}$ ion. Hence, neptunium(VII), like Np(V) and Np(VI), is in a tetragonal–bipyramidal environment formed by oxygen atoms due to which the electron transfer is not accompanied by a substantial structural rearrangement of the ions involved in the reaction. The position of the equilibrium depends on the alkali concentration. In a 7.8 M NaOH solution (at 24 °C), the equilibrium constant

$$K = \frac{[Np(VII)][Pu(V)]}{[Np(VI)][Pu(VI)]}$$

is 1.8×10^{-2}; its value increases to 14×10^{-2} as the NaOH concentration is increased to 10.1 mol litre^{-1}.

b. Reactions of Np(VI) with Am(VI) and Am(VII)
Neptunium(VII) is rapidly formed upon the addition of a bicarbonate or weakly acidic Am(VI) solution to a 1 M NaOH solution containing Np(VI) (see Ref. 36)

$$Np(VI) + Am(VI) \rightleftharpoons Np(VII) + Am(V). \quad (99)$$

The position of the reaction equilibrium depends on the concentration of the OH^- ions. Oxidation of Np(VI) starts at $[OH^-] \approx 0.016$ mol litre^{-1}. The yield of Np(VII) increases as the alkali concentration is increased and it reaches 100% in 3–4 M NaOH solutions. Americium(V) does not react with Np(VI) in alkaline solutions.

The addition of a cooled freshly prepared (by ozonation) Am(VII) solution in 3–4 M NaOH to an alkaline solution of Np(VI) rapidly affords Np(VII)[101, 102]

$$2\,Np(VI) + Am(VII) \longrightarrow 2\,Np(VII) + Am(V). \quad (100)$$

c. Reactions of Pu(VI) with Am(VI) and Am(VII)
The equilibrium of the reaction

$$Pu(VI) + Am(VI) \rightleftharpoons Pu(VII) + Am(V) \quad (101)$$

is established immediately after mixing the reagents,[36] but is is noticeably shifted to the right only at an alkali concentration higher than 7.5 mol litre^{-1}. Plutonium(VII) is virtually immediately formed upon the addition of freshly prepared (by ozonation) Am(VII) to a 1 M NaOH solution containing Pu(VI)[101, 102]

$$Pu(VI) + Am(VII) \rightleftharpoons Pu(VII) + Am(VI). \quad (102)$$

3. Oxidation reactions

a. Oxidation with molecular oxygen
Neptunium(V) and plutonium(V). Oxygen bubbling through 0.5–2 M LiOH or NaOH solutions containing neptunium(V) for 24 h did not yield Np(VI). As the alkali concentration and the reaction time were increased, Np(V) was slowly transformed into Np(VI) under the action of both pure O_2 and atmospheric oxygen.[103] In an aerated 8 M NaOH solution containing Np(V) (1 mmol litre^{-1}), ~10% of Np(V) was oxidised during 3 months. In the same solution containing F^- (0.1 mol litre^{-1}), ~50% of Np(V) was oxidised during one month. A change in the temperature of the solution from 0 to 50 °C exerts only a slight effect on the kinetics of Np(V) oxidation.

Plutonium(V) is also oxidised with atmospheric oxygen in 4 M and 8 M NaOH solutions. In the latter case, the rate constant of the reaction (1.4×10^{-3} h^{-1}) is smaller than the rate constant of Np(V) oxidation (4.7×10^{-3} h^{-1}), whereas plutonium(V) in a 4 M NaOH solution is oxidised faster than Np(V). This is, apparently, associated with a change in the reaction mechanism. Most likely, oxygen reacts with Pu(IV) that is generated through disproportionation of Pu(V).

Neptunium(IV) and plutonium(IV). A freshly precipitated suspension of neptunium(IV) hydroxide [we will denote this compound and plutonium(IV) hydroxide as $NpO_2 \cdot n\,H_2O$ and $PuO_2 \cdot n\,H_2O$, respectively] is slowly oxidised with oxygen.[104] At 23 °C, a suspension of $NpO_2 \cdot n\,H_2O$ (7 mmol litre^{-1}) in 2–14 M NaOH solutions is completely oxidised during ~1–2 days. In addition to neptunium(V), Np(VI) is formed in substantial amounts. As the alkali concentration is increased, the reaction slightly slows down and the proportion of Np(VI) is decreased.

It is believed that oxygen is adsorbed on the surface of Np(IV) hydroxide species followed by successive or synchronous electron transfer. The intermediate that formed in the course of O_2 reduction (hydrogen peroxide) is not accumulated in solution.

A suspension of $PuO_2 \cdot n\,H_2O$ in 0.5–4 M NaOH solutions does not react with oxygen. Prolonged air bubbling through a 5 M NaOH solution containing this suspension affords different ionic forms of plutonium whose concentration is 10% higher than that obtained upon argon bubbling.[104]

b. Oxidation with hydrogen peroxide
Neptunium(IV). The addition of H_2O_2 (100 mmol litre^{-1}) to a 0.5 M NaOH solution containing a $NpO_2 \cdot n\,H_2O$ suspension (10 mmol litre^{-1}) at 20 °C gave rise to a dissolved Np(V) peroxide complex. Oxidation of Np(IV) was completed in less than 10 min. Then Np(V) gradually precipitated.[105]

In NaOH 1–16 M solutions, the formation of Np(V) starts once the reagents have been mixed but the reaction rate decreases as the NaOH concentration is increased. The Np(V) peroxide complex is stable over a long period and the solid phase does not appear for at least 3 h.[105]

The formation of Np(V) slows down as the H_2O_2 concentration is decreased. At $[H_2O_2] = 5$ mmol litre^{-1}, 9% of Np(IV) remains in the precipitate after completion of the reaction. Taking into account that hydrogen peroxide in an alkaline medium exists as the HO_2^- ion, it may be written

$$2\,NpO_2\cdot n\,H_2O + HO_2^- \longrightarrow 2\,NpO_2OH + OH^- + m\,H_2O. \quad (103)$$

Decomposition of H_2O_2 proceeds as a competitive reaction.

The formation of Np(V) (and precipitation) is accelerated as the temperature is increased from 20 to 60 °C.

Plutonium(IV). When a 1 M NaOH solution containing a freshly precipitated $PuO_2\cdot n\,H_2O$ suspension (1 mmol litre^{-1}) and H_2O_2 (10 mmol litre^{-1}) was kept at 20 °C for 7 h, the concentration of plutonium in the ionic form remained the same as that in a check experiment performed in the absence of H_2O_2. In more concentrated alkaline solutions, the higher is the NaOH concentration, the higher is the rate of Pu(IV) oxidation. Thus in a 12 M NaOH solution containing $PuO_2\cdot n\,H_2O$ (10 mmol litre^{-1}) and H_2O_2 (50 mmol litre^{-1}), the Pu(V) peroxide complex was detected in an amount of 0.4 mmol litre^{-1} already after 8 min.[105]

Slow oxidation of Pu(IV) with hydrogen peroxide in a 1 M NaOH solution takes place upon the addition of a trivalent iron salt (to the concentration of 0.1 mol litre^{-1}). The addition of Co(II) and Cu(II) salts has a weaker effect on oxidation of Pu(IV) with hydrogen peroxide. No effect of Ni(II) was observed.[105]

Americium(III). Oxidation of $Am(OH)_3$ to Am(IV) under the action of hydrogen peroxide was first presented in the paper.[106] These data are confirmed by the results of a more detailed study.[107] An acidic solution of Am(III) containing H_2O_2 was neutralised with ammonia. The precipitate that formed [presumably, Am(III) hydroperoxide] was treated with a concentrated ammonia or KOH solution to obtain Am(IV) hydroxide. The process was accelerated upon heating to 90 °C. At this temperature, Am(IV) hydroxide was obtained in quantitative yield according to several procedures:

— by treatment of $Am(OH)_3$ with a H_2O_2 and KOH solution;

— by treatment of Am(III) hydroperoxide with a H_2O_2 and KOH solution;

— by treatment of Am(III) hydroperoxide with a KOH solution.

c. Oxidation with ozone

Neptunium(VI) and neptunium(V). Neptunium(VII) was first prepared by oxidation of a suspension of sodium or potassium neptunates with ozone in 0.5–3.5 M alkaline solutions.[108,109] The kinetics of the reaction of ozone with Np(VI) depends on the state of the latter. In the case of ozonation of neptunate suspensions in NaOH (or KOH) solutions, the rate of Np(VII) formation depends on the mode of ozone supply and the properties of the solid phase. Thus, the rate of Np(VI) oxidation is decreased upon prolonged storage of the precipitates. In the study,[14] it was suggested that a suspension of Np(V) hydroxide in NaOH solutions be used in these reactions. In the course of ozonation, Np(V) is oxidised to soluble Np(VI), which is transformed into the heptavalent state. The maximum concentration of Np(VII) obtained in NaOH (or KOH) solutions is 6–8 g litre^{-1}. The Np(VII) content of 30 g litre^{-1} was achieved upon ozonation of neptunates in 2–3 M LiOH solutions[110] due to high solubility of lithium neptunates.[111]

The kinetics of Np(VII) formation in alkaline solutions containing Np(VI) ions is determined by the rate of ozone supply and intensity of stirring, *i.e.*, by diffusion factors.[109,112,113] At low concentrations of the reagents, the reaction of Np(VI) with O_3 is kinetically controlled. The accumulation of Np(VII) obeys the equation[112]

$$\frac{d[Np(VII)]}{dt} = k[Np(VI)][OH^-]^{0.5}[O_3]^{0.5}. \quad (104)$$

In the temperature range of 0–20 °C, the activation energy is close to 20 kJ mol^{-1}.[112]

An analogous dependence of the rate of Np(VII) accumulation on the ozone concentration was found in the study.[113] In a solution with a constant LiOH concentration, the rate of oxidation (V) of Np(VI) (10 mmol litre^{-1}) at a constant rate of ozone supply remains unchanged, *i.e.*,

$$V = \frac{d[Np(VII)]}{dt} = \text{const}. \quad (105)$$

The plot of V *vs.* the LiOH concentration yields a curve with a maximum at $[OH^-] \approx 1.5$–2 mol litre^{-1}. It was proposed that the $OH^\bullet$ radical[112] or the $O^{-\bullet}$ radical ion[113] serve as a direct oxidiser of Np(VI). However, in our opinion, the $O_3^{-\bullet}$ radical ion[114] serves as an oxidiser. Thus as the LiOH concentration is lowered beyond 1 mol litre^{-1}, the rate of Np(VI) oxidation decreases due to acceleration of $O_3^{-\bullet}$ decomposition giving rise to $O_2^{-\bullet}$.

Neptunium(VI) is oxidised with ozone even at pH 9–10 although the reaction rate is noticeably lower.[115] Moreover, heptavalent neptunium is partially generated upon ozonation of a NpO_2OH suspension in water.[116]

The completeness of Np(VI) oxidation with ozone in alkaline solutions depends on its concentration. For example, Np(VI) was oxidised by 80% at its concentration of $(2–4)\times10^{-5}$ mol litre^{-1},[112] whereas 98%–100% of Np(VI) was oxidised at the concentration of 3×10^{-3} mol litre^{-1}.[113]

Neptunium(IV). When a mixture of O_2 and O_3 (0.7 vol.%) is passed through 0.5–1 M NaOH solutions containing a suspension of $NpO_2\cdot n\,H_2O$ (1 mmol litre^{-1}), neptunium(IV) is oxidised to Np(V) and Np(VI) already within minutes after the onset of the process and the suspension is dissolved. Further ozonation affords Np(VII). Accumulation of Np(VII) is accelerated as the alkali concentration is increased. In a 14 M NaOH solution, neptunium is quantitatively transformed into the heptavalent state already within 8 min after the onset of oxidation.[104]

Ozone can directly oxidise tetra-, penta- and hexavalent neptunium. However, in a strongly alkaline medium, ozone initially reacts with the OH^- ions to form the ozonide ions. In this case, the reactions may be described by the scheme[117]

$$O_3 + OH^- \longrightarrow O_3^{-\bullet} + OH^\bullet, \quad (106)$$

$$OH^\bullet + OH^- \rightleftharpoons O^{-\bullet} + H_2O, \quad (107)$$

$$O^{-\bullet} + O_2 \longrightarrow O_3^{-\bullet}, \quad (108)$$

or the scheme[118]

$$O_3 + OH^- \longrightarrow O_2 + HO_2^-, \quad (109)$$

$$O_3 + HO_2^- \longrightarrow O_3^{-\bullet} + HO_2^\bullet. \quad (110)$$

$$HO_2^\bullet + OH^- \longrightarrow O_2^{-\bullet} + H_2O, \quad (57)$$

$$O_3 + O_2^{-\bullet} \longrightarrow O_3^{-\bullet} + O_2. \quad (111)$$

The ozonide ions oxidise all valence forms of neptunium to the heptavalent state. The process starts with the reaction

$$NpO_2\cdot n\,H_2O + O_3^{-\bullet} \longrightarrow NpO_2(OH) + O_2 + OH^- + m\,H_2O. \quad (112)$$

Neptunium(V) is oxidised both in the solid phase and after the formation of the soluble $NpO_2(OH)_n^{1-n}$ complex ($n = 2$–3). In this case, the following reactions proceed

$$NpO_2(OH)_n^{1-n} + O_3^{-\bullet} + H_2O \longrightarrow \quad (113)$$

$$\longrightarrow NpO_2(OH)_4^{2-} + O_2 + (n-2)\,OH^-,$$

$$NpO_2(OH)_4^{2-} + O_3^{-\bullet} \longrightarrow NpO_4(OH)_2^{3-} + O_2 + H_2O \quad (114),$$

the rate constants are $(2.1\pm0.3)\times10^6$ and $(2.1\pm0.2)\times10^5$ litre mol^{-1} s^{-1}, respectively.[114]

Accumulation of Np(VII) occurs after the disappearance of Np(IV) and Np(V).

Plutonium(VI). Like Np(VII), heptavalent plutonium was first prepared by ozonation.[108, 119] Presently, this procedure is commonly used for the preparation of pure Pu(VII) solutions with different concentrations.

The reaction of Pu(VI) with O_3 in alkaline media proceeds analogously to the reaction of Np(VI).[113] In homogeneous solutions, the reaction rate is determined by the diffusion factors. In the mode of steady ozone supply, the rate of this reaction is described by the zero-order equation

$$V = \frac{d[Pu(VII)]}{dt} = \text{const.} \quad (115)$$

The completeness of oxidation of Pu(VI) (7.5 mmol litre^{-1}) in alkaline solutions ([NaOH] < 1 mol litre^{-1}) depends on instability of Pu(VII) whose reduction with water is accelerated as the concentration of the OH^- ions is decreased.[120]

Plutonium(IV). Oxidation of Pu(IV) with ozone was examined in the study.[104] A suspension of $PuO_2 \cdot n H_2O$ (0.3–0.5 mmol litre^{-1}) in a 0.5–8 M NaOH solution was oxidised with a mixture of O_2 and O_3 (0.7 vol.%). The resulting Pu(VII) and Pu(VI) rapidly reacted with Pu(IV). Hence, accumulation of Pu(VII) becomes possible after the complete disappearance of Pu(IV). In a 1 M NaOH solution, Pu(VII) is formed most rapidly (84 min), whereas the time of this reaction increases to 300 min (and more) in an 8 M NaOH solution.

The oxidation process involves the reactions (106)–(108) and reactions analogous to (112)–(114).

Americium(VI). When a gas mixture containing O_3 (20–50 mg litre^{-1}) was passed through a cooled (0 °C) solution of americium(VI) in 3–4 M NaOH during 30–60 min, the colour and absorption spectrum of the solution were changed.[101, 102] After the addition of the resulting freshly ozonated alkaline solution of americium to an excess of Pu(VI) in 1 M NaOH, plutonium immediately took on the colour characteristic of Pu(VII). The absorption spectrum of the resulting solution agrees satisfactorily with the absorption spectrum of pure Pu(VII).

It is known [37] that Am(VI) does not oxidise Pu(VI) in solutions containing NaOH at a concentration lower than 3 mol litre^{-1}. Hence, the formation of Pu(VII) in the experiments described above indicates that americium(VI) is transformed into Am(VII) upon ozonation of its alkaline solutions. Heptavalent americium reacts with Pu(VI) according to Eqn (102). The yield of Am(VII) upon ozonation can be estimated from the amount of Pu(VII) formed. In different experiments, its value varied from 40% to 60%. The same results were obtained in the study of the stoichiometry of the reaction (100).

Americium(III). Oxidation of Am(III) was examined in a wide pH range.[121] Ozone oxidises $Am(OH)_3$ to Am(VI) both in neutral and alkaline (1 M NaOH) media. In a 1 M NaOH solution, oxidation proceeds slowly. Therefore, it is necessary to lower the temperature to 0 °C for the enhancement of solubility of O_3. In a 0.1 M NaOH solution (at 25 °C), $Am(OH)_3$ is oxidised with a moderate rate to form Am(VI), which gives a soluble yellow complex. The absorption spectrum of this complex is identical to the spectrum of the solution, which was prepared by adding alkali to an acidic solution of AmO_2^{2+}. In water, Am(III) is oxidised by passing ozone for 1–2 h (T = 90 °C). In the course of ozonation, pH of the solution must be no lower than 5.

Apparently, the mechanism of Am(III) oxidation in solutions with pH lower than 12 is analogous to the mechanism of oxidation in carbonate solutions. This mechanism involves the inner-sphere transfer of the oxygen atom from O_3 as the first step. The general scheme of oxidation is as follows:

$$Am(OH)_3 + O_3 \longrightarrow AmO_2OH + O_2 + H_2O, \quad (116)$$

$$AmO_2OH + O_3 + OH^- \longrightarrow AmO_2(OH)_2 + O_3^{-\bullet}, \quad (117)$$

$$Am(OH)_3 + O_3^{-\bullet} + H_2O \longrightarrow AmO_2 \cdot n H_2O + O_2 + OH^-, \quad (118)$$

$$AmO_2 \cdot n H_2O + O_3 \longrightarrow AmO_2(OH)_2 + O_2 + (n-1) H_2O. \quad (119)$$

In alkaline solutions (pH > 12), the reactions (106)–(108), (118) and (119) and also the reaction

$$AmO_2 \cdot n H_2O + O_3^{-\bullet} \longrightarrow \quad (120)$$
$$\longrightarrow AmO_2OH + O_2 + (n-1) H_2O + OH^-$$

are the major processes.

Americium(V) is oxidised in both the solid phase and in the dissolved form existing as the $AmO_2(OH)_n^{1-n}$ complex (n = 2–3)

$$AmO_2(OH)_n^{(1-n)} + O_3^{-\bullet} + H_2O \longrightarrow \quad (121)$$
$$\longrightarrow AmO_2(OH)_4^{2-} + O_2 + (n-2) OH^-.$$

At 0 °C, Am(VII) is formed in 3–4 M NaOH solutions

$$AmO_2(OH)_4^{2-} + O_3^{-\bullet} \longrightarrow Am(VII) + O_2. \quad (122)$$

d. Oxidation with $S_2O_8^{2-}$ ions

Neptunium(VI). The kinetics of Np(VI) oxidation was examined in 0.1–0.7 M NaOH solutions at T > 50 °C.[122] The initial reaction rate did not depend on the Np(VI) concentration (up to 0.3 mmol litre^{-1}) and increased in directly proportion to the $S_2O_8^{2-}$ concentration (the latter was increased from 25 to 300 mmol litre^{-1})

$$\frac{d[Np(VII)]}{dt} = -\frac{d[Np(VI)]}{dt} = k[S_2O_8^{2-}]. \quad (123)$$

In a 0.2 M NaOH solution heated to 60 °C, the rate constant of the reaction is 2×10^{-4} min^{-1}. At [OH^-] = 0.7 mol litre^{-1} and μ = 1, the activation energy is 140 kJ mol^{-1}, which is consistent with the activation energy of thermal decomposition of the persulfate ions.[57]

The first step of Np(VI) oxidation with the persulfate ions in 0.2–0.7 M NaOH solutions involves decomposition of the $S_2O_8^{2-}$ ions [reaction (32)] followed by the reaction

$$SO_4^{-\bullet} + OH^- \longrightarrow SO_4^{2-} + OH^{\bullet}. \quad (124)$$

The fast reactions (124), (107) and (108) afford the $O_3^{-\bullet}$ radical ions, which oxidise Np(VI) to Np(VII) according to the reaction (114).

Calculations demonstrated that the rate of Np(VII) accumulation in a NaOH solution is three times lower than the rate of formation of the $SO_4^{-\bullet}$ radical ions. Consequently, decomposition of $O_3^{-\bullet}$ is of considerable importance in this process, as in the case of Np(VI) oxidation with ozone at [OH^-] < 1 mol litre^{-1}. The rate of Np(VII) accumulation decreases as the alkali concentration is increased to 0.9 mol litre^{-1}. The plot of Np(VII) accumulation in a 1 M NaOH solution (μ = 2) goes through a maximum. In 3–4 M NaOH solutions, neptunium(VII) is not formed at all.

Apparently, decomposition of $S_2O_8^{2-}$ in alkaline solutions proceeds not only through thermal decomposition [reaction (32)] but also under the action of the OH^- ions, reducers being formed in the latter case. This pathway becomes dominant in 3–4 M NaOH solutions. On a further increase in the alkali concentration to 5–6 mol litre^{-1}, the formation of Np(VII) resumes. Under these conditions, the mechanism of decomposition of persulfate ions is, evidently, changed once again. An increase in the ionic strength of solution has virtually no effect on the rate of Np(VI) oxidation in a 0.2 M NaOH solution but the reaction rate is decreased in a 0.7 M NaOH solution.

Hydroxides of some d elements serve as catalysts of the Np(VII) formation. In a 4 M NaOH solution, the $S_2O_8^{2-}$ ions oxidise N(VI) even at 20 °C in the presence of Fe(III), Ag(I), Cu(II), Ni(II) or Co(II) salts in concentrations of 5×10^{-5}, 1×10^{-5}, 5×10^{-6}, 1×10^{-7} or 2×10^{-8} mol litre^{-1}, respectively. In alkaline solutions containing Ni(II) or Co(II) com-

pounds, Np(VII) is completely reduced during 15–20 h. After storage for one day, silver(I) salts retain catalytic activity.

In a 0.5 M NaOH solution, the catalytic activity of the *d*-metal ions is less pronounced.

In the temperature range of 30–50 °C, the activation energies of Np(VI) oxidation in the presence of the Ag(I) and Co(II) ions are 67 and 42 kJ mol^{-1}, respectively.

Neptunium(IV). In deaerated 0.5–14 M NaOH solutions containing a suspension of hydrated Np(IV) oxide (7 mmol litre^{-1}), Np(V), Np(VI) and Np(VII) are successively accumulated under the action of $S_2O_8^{2-}$.[123] All steps of oxidation are accelerated as the concentrations of NaOH and $S_2O_8^{2-}$ are increased and the temperature is raised. In a 4 M NaOH solution containing $S_2O_8^{2-}$ (20 mmol litre^{-1}), the transformation of neptunium(IV) into the dissolved Np(VI) form proceeds by 95% at 21 °C during 11–12 min. After the next 5–7 min, Np(VII) is generated. In a 4 M NaOH solution, the activation energy of Np(VI) oxidation with persulfate ions is 68 kJ mol^{-1}. In the presence of insufficient persulfate, Np(V) and Np(VI) were found in the solution (T = 36 °C) after completion of the reaction.

The oxidation process involves the following reactions [Np(V) and Np(VI) react both in the solid and liquid phases after the formation of soluble complexes]:

$$Np(IV) + S_2O_8^{2-} \longrightarrow Np(V) + SO_4^{-\bullet} + SO_4^{2-}, \quad (125)$$

$$Np(V) + S_2O_8^{2-} \longrightarrow Np(VI) + SO_4^{-\bullet} + SO_4^{2-}, \quad (35)$$

$$Np(VI) + S_2O_8^{2-\bullet} \longrightarrow Np(VII) + SO_4^{-\bullet} + SO_4^{2-}. \quad (40)$$

Then, the reactions (124), (107), (108) and (112)–(114) proceed.

Plutonium(VI). It was found[124] that the reaction of Pu(VI) (0.75 mmol litre^{-1}) with the $S_2O_8^{2-}$ ions in KOH solutions afforded Pu(VII), which was accumulated according to the kinetic equation (reaction is zero order with respect to plutonium and first order with respect to $S_2O_8^{2-}$)

$$\frac{d[Pu(VII)]}{dt} = -\frac{d[Pu(VI)]}{dt} = k[S_2O_8^{2-}]. \quad (126)$$

In a 1 M KOH solution, the activation energy of Pu(VI) oxidation is 146 kJ mol^{-1}, which is similar to the activation energy of thermal decomposition of the persulfate ions. Oxidation proceeds with the participation of the $O_3^{-\bullet}$ radical ions [see the reactions (32), (124), (107) and (108)]

$$PuO_2(OH)_4^{2-} + O_3^{-\bullet} \longrightarrow PuO_4(OH)_2^{3-} + O_2 + H_2O. \quad (127)$$

In hot KOH solutions containing the $S_2O_8^{2-}$ ions, oxidation of Pu(VI) is accompanied by reduction of Pu(VII). As the KOH concentration is increased from 0.2 to 1.2 mol litre^{-1} ([$S_2O_8^{2-}$] = 0.1 mol litre^{-1}, T = 80 °C), the rate of Pu(VII) accumulation initially somewhat increases, peaks at the KOH concentration of 0.5 mol litre^{-1} and then decreases. The yield of Pu(VII) {the [Pu(VII)]/[Pu(VI)]$_0$ ratio} is linearly increased as the KOH concentration is increased to ~1 mol litre^{-1} and then is sharply decreased. At a low alkali concentration, the rate of Pu(VII) reduction with water increases and, hence, its yield is decreased under these conditions. An increase in the KOH concentration leads to the enhancement of stability of Pu(VII) and an increase in its yield. In solutions with [KOH] > 1 mol litre^{-1}, oxidation of Pu(VI) ceases. This is attributed to catalytic decomposition of $S_2O_8^{2-}$ to form reducers. One would expect a change in these dependences at other temperatures and concentrations of persulfate ions.

Plutonium(IV). Hexavalent plutonium is accumulated in 0.5–8 M NaOH solutions containing a suspension of freshly precipitated hydrated Pu(IV) oxide and $S_2O_8^{2-}$ (10–50 mmol litre^{-1}). At [NaOH] $\geqslant$ 4 mol litre^{-1}, Pu(VII) is also generated.[125] The rate of dissolution of hydrated Pu(IV) oxide increases as the concentrations of NaOH and $S_2O_8^{2-}$ are increased and the temperature is raised from 23 to 62 °C. The following solid-phase reactions are of importance in oxidation and dissolution:

$$Pu(IV) + S_2O_8^{2-} \longrightarrow Pu(V) + SO_4^{-\bullet} + SO_4^{2-}, \quad (128)$$

$$Pu(V) + S_2O_8^{2-} \longrightarrow Pu(VI) + SO_4^{-\bullet} + SO_4^{2-}. \quad (129)$$

Simultaneously with these reactions, Pu(V) goes into the solution where it is also oxidised to Pu(VI) and undergoes disproportionation. Plutonium(VI) reacts with $PuO_2 \cdot n H_2O$. In 4–8 M NaOH solutions, Pu(VI) is oxidised

$$Pu(VI) + S_2O_8^{2-} \longrightarrow Pu(VII) + SO_4^{-\bullet} + SO_4^{2-}. \quad (130)$$

In addition, $O_3^{-\bullet}$ is formed under these conditions and reactions involving this radical proceed.

Americium(III). Oxidation of $Am(OH)_3$ (a pink suspension) with the $S_2O_8^{2-}$ ions in an alkaline medium affords a black or dark-brown precipitate of hydrated Am(IV) oxide.[106] The reaction of $Am(OH)_3$ (5 mg) with excess $K_2S_2O_8$ in a 0.1 M NaOH solution on a boiling water bath (2 h) gave rise to an olive-brown precipitate. The examination of products of its dissolution in acid demonstrated[121] that the average oxidation number of americium is 4.53, *i.e.*, the precipitate contains not only Am(IV) but also americium in higher oxidation states.

Pure Am(IV) was prepared by adding Am(III) to a hot 7 M KOH solution saturated with $K_2S_2O_8$. Then the reaction mixture was kept at 90 °C for 1 h. The precipitate was washed with water to remove an excess of the oxidiser. The average oxidation state of americium in hydrated oxide is 4.0 ± 0.1.[121]

e. Oxidation with ClO^- ions

Neptunium(IV). In deaerated 0.5–16 M NaOH solutions containing $NpO_2 \cdot n H_2O$, the successive formation of Np(V), Np(VI) and Np(VII) takes place under the action of the ClO^- ions.[126] The time dependence of the Np(VI) concentration in solution passes through a maximum. Initially, a supersaturated solution of Np(VI) is formed from which Np(VI) hydroxide gradually precipitates. Neptunium(VII) is formed in a 2 M NaOH solution (T = 25 °C) at [ClO^-] = 48 mmol litre^{-1}. In more concentrated alkaline solutions, a lower concentration of the hypochlorite ions is sufficient for the formation of Np(VII). The activation energy of the Np(VII) formation is 34 kJ mol^{-1} (T = 25–60 °C). The oxidation reactions of Np(IV), Np(V) and Np(VI) are accelerated as the temperature is raised and the concentrations of alkali and hypochlorite ions are increased.

The oxidation process involves the following steps:

$$NpO_2 \cdot n H_2O + OH^- + ClO^- \longrightarrow NpO_2(OH) + ClO^{2-\bullet} + m H_2O, \quad (131)$$

$$NpO_2 \cdot n H_2O + ClO^{2-\bullet} \longrightarrow NpO_2(OH) + Cl^- + OH^- + m H_2O. \quad (132)$$

It is not improbable that Np(IV) is oxidised due to the transfer of the oxygen atom taking into account that oxygen is involved in the oxygenated Np(V) and Np(VI) ions

$$NpO_2 \cdot n H_2O + ClO^- \longrightarrow NpO_2(OH)_2 + Cl^- + (n-1) H_2O. \quad (133)$$

Then the reaction (10) proceeds in the precipitate.

The mechanism of neptunium oxidation can be conclusively established with the use of the ^{18}O-labelled hypochlorite ions.

In a precipitate, neptunium(V) reacts with ClO^-

$$NpO_2OH + ClO^- + OH^- \longrightarrow NpO_2(OH)_2 + ClO^{2-\bullet}, \quad (134)$$

$$NpO_2OH + ClO^{2-\bullet} + H_2O \longrightarrow NpO_2(OH)_2 + Cl^- + OH^-. \quad (135)$$

In solution, the latter reaction proceeds differently

$$NpO_2(OH)_2^- + ClO^{2-\bullet} + OH^- \longrightarrow NpO_2(OH)_4^{2-} + Cl^-. \quad (136)$$

Neptunium(VI) is, in turn, oxidised to Np(VII)

$$NpO_2(OH)_4^{2-} + ClO^- + 2\,OH^- \longrightarrow \quad (137)$$
$$\longrightarrow NpO_4(OH)_2^{3-} + ClO^{2-\bullet} + 2\,H_2O,$$

$$NpO_2(OH)_4^{2-} + ClO^{2-\bullet} \longrightarrow NpO_4(OH)_2^{3-} + Cl^- + H_2O. \quad (138)$$

Reproportionation of Np(VII) and Np(V) [reaction (94)] occurs in a dilute alkaline solution, and disproportionation of Np(VI) takes place in 9–16 M NaOH solutions.

Neptunium(VI). In 1–4 M LiOH solutions or 1–8.5 M NaOH solutions, neptunium(VI) is oxidised with K_2IrCl_6.[127]

$$Np(VI) + IrCl_6^{2-} \longrightarrow Np(VII) + IrCl_6^{3-}. \quad (139)$$

Neptunium(VII) thus prepared slowly disappears because $IrCl_6^{3-}$ is hydrolysed and the resulting Ir(III) hydroxide reduces Np(VII).

The addition of a NaClO solution to an alkaline solution of neptunium(VI) containing iridium hydroxides leads to the slow formation of Np(VII) because iridium is transformed into higher oxidation states under the action of the ClO^- ions. The $ClO^{2-\bullet}$ radical ions that are formed react with Np(VI) [see the reaction(138)].

Plutonium(IV). The hypochlorite ions oxidise a suspension of freshly prepared $PuO_2 \cdot n\,H_2O$ even at room temperature.[126] In a precipitate, plutonium is transformed into a hexavalent state. Plutonium(VI) remains partially in solution. Plutonium(VII) appears at the NaOH concentration of about 10 mol litre^{-1}. The rate and completeness of dissolution of Pu(IV) (6.8 mmol litre^{-1}; 60 °C, $[ClO^-] = 12$ mmol litre^{-1}) are increased as the NaOH concentration is increased. In a 8 M NaOH solution, 92%–94% of plutonium is dissolved. The initial rate of accumulation of plutonium in solution increases as the ClO^- concentration and temperature are increased.

Oxidation of Pu(IV) proceeds analogously to oxidation of Np(IV) and involves the reactions

$$PuO_2 \cdot n\,H_2O + OH^- + ClO^- \longrightarrow \quad (140)$$
$$\longrightarrow PuO_2(OH) + ClO^{2-\bullet} + m\,H_2O,$$

$$PuO_2 \cdot n\,H_2O + ClO^{2-\bullet} \longrightarrow \quad (141)$$
$$\longrightarrow PuO_2(OH) + Cl^- + OH^- + (n-1)\,H_2O,$$

which take place in the solid phase. In 0.4–1.5 M NaOH solutions, plutonium(V) either undergoes disproportionation or is oxidised

$$PuO_2(OH) + ClO^- + OH^- \longrightarrow PuO_2(OH)_2 + ClO^{2-\bullet}, \quad (142)$$

$$PuO_2(OH) + ClO^{2-\bullet} + H_2O \longrightarrow \quad (143)$$
$$\longrightarrow PuO_2(OH)_2 + Cl^- + OH^-.$$

Plutonium(V) and Pu(VI) partially go into solution where they are further oxidised

$$PuO_2(OH)_4^{2-} + ClO^- + 2\,OH^- \longrightarrow \quad (144)$$
$$\longrightarrow PuO_4(OH)_2^{3-} + ClO^{2-} + 2\,H_2O,$$

$$PuO_2(OH)_4^{2-} + ClO^{2-\bullet} \longrightarrow PuO_4(OH)_2^{3-} + Cl^- + H_2O. \quad (145)$$

Oxidation of Pu(IV) can also occur through the transfer of the oxygen atom from ClO^-

$$PuO_2 \cdot n\,H_2O + ClO^- \longrightarrow PuO_2(OH)_2 + Cl^- + (n-1)\,H_2O. \quad (146)$$

Americium(III). Precipitation of a pink suspension of Am(III) in an alkaline solution containing ClO^- afforded a dark precipitate.[128] This process was studied in detail.[121] In a 0.2 M NaOH solution containing ClO^- (0.2 mol litre^{-1}), $Am(OH)_3$ was transformed into hydrated Am(IV) oxide at 100 °C during 30 min.

f. Oxidation with BrO^- ions

Neptunium(VI). In alkaline solutions containing Np(VI) (0.2 mmol litre^{-1}), neptunium(VI) is oxidised with the hypobromite ions upon heating to 70 °C.[129] In 1.74–6.5 M NaOH solutions, the kinetics of the reaction is described by the empirical equation[130]

$$\frac{d[Np(VII)]}{dt} = -\frac{d[Np(VI)]}{dt} = k[Np(VI)][BrO^-]^{0.6}[OH^-]^{1.6}, \quad (147)$$

where $k = (6.65 \pm 0.35) \times 10^{-2}$ litre$^{2.2}$ mol$^{-2.2}$ min^{-1} at 70 °C. In a 6.5 M NaOH solution, the activation energy of the reaction is 87.5 kJ mol^{-1} ($T = 50.7$–70 °C).

The rate of Np(VI) oxidation with the BrO^- ions depends on the OH^- concentration in a complicated manner, which reflects both the participation of hydroxyl ions in the formation of an activated complex and the effect of the ionic strength of solution. The fractional order of the reaction with respect to the BrO^- ions results from the fact that the processes

$$NpO_2(OH)_4^{2-} + BrO^- + 2\,OH^- \longrightarrow \quad (148)$$
$$\longrightarrow NpO_4(OH)_2^{3-} + BrO^{2-\bullet} + 2\,H_2O,$$

$$NpO_2(OH)_4^{2-} + BrO^{2-\bullet} \longrightarrow NpO_4(OH)_2^{3-} + Br^- + H_2O \quad (149)$$

are accompanied by the reactions of Np(VI) with radical products of BrO^- decomposition.

Oxidation of Np(VI) with the hypobromite ions is accelerated upon the addition of *d*-metal salts. In dilute alkali (0.5 mol litre^{-1}), the formation of Np(VII) was observed only in the presence of 2.5×10^{-5} mol litre^{-1} of Cu(II) or $(1-5) \times 10^{-6}$ mol litre^{-1} of Ni(II) or Co(II).

Neptunium(IV). In deaerated 0.8–16 M NaOH solutions containing a suspension of $NpO_2 \cdot n\,H_2O$ (5 mmol litre^{-1}), Np(V), Np(VI) and Np(VII) are formed in the presence of BrO^-.[131] At 25 °C, the rate of Np(VII) accumulation is approximately proportional to the NaOH concentration and the process is accelerated as the BrO^- concentration is increased. In the temperature range of 25–40 °C, the activation energy of this reaction is 32 kJ mol^{-1}. Oxidation is most likely to occur according to the reactions analogous to the reactions (131)–(136) followed by the reactions (10), (148) and (149).

Plutonium(VI). Oxidation of Pu(VI) (0.85 mmol litre^{-1}) with the hypobromite ions was studied in 10.4–12.4 M KOH solutions at 50–90 °C.[124] The completeness and rate of oxidation are increased as the concentrations of alkali and KBrO are increased (7–100 mmol litre^{-1}). The initial regions of the kinetic plots yield straight lines, which are indicative of oxidation of Pu(VI) with radical products. The activation energy, which we estimated from the results of the study,[124] is 45–50 kJ mol^{-1}.

The addition of Co(II) and Ni(II) salts to 10^{-5} mol litre^{-1} leads to substantial acceleration of BrO^- decomposition and Pu(VII) accumulation, which suggests that these processes correlate with each other.

Plutonium(IV). In 0.8–16 M NaOH solutions containing a suspension of $PuO_2 \cdot n\,H_2O$, Pu(VI) is accumulated both in the precipitate and solution under the action of the hypobromite ions.[131] Plutonium(VII) is formed in 12–16 M NaOH solutions. The rates of all steps increase as the concentrations of alkali and the oxidiser are increased. The activation energy of the Pu(VI) formation in solution is 23 kJ mol^{-1} and the activation energy of the Pu(VII) formation in a 16 M NaOH solution is ~35 kJ mol^{-1}. Oxidation of plutonium(IV) proceeds analogously to oxidation of neptunium(IV).

g. Oxidation with $Fe(CN)_6^{3-}$ ions

Neptunium(VI). The reaction

$$Np(VI) + Fe(CN)_6^{3-} \rightleftharpoons Np(VII) + Fe(CN)_6^{4-} \quad (150)$$

is reversible and its equilibrium depends substantially on the concentration of the hydroxyl ions. In 1–4 M KOH solutions, the equilibrium constant is proportional to $[OH^-]^4$, whereas this constant in solutions with $\mu = 4$ is proportional to $[OH^-]^3$.[93] In a 3.2 M KOH solution, the equilibrium constant (at 23 °C) is 2.0 ± 0.2. At the concentrations of the reagents of ~ 0.1 mmol litre^{-1}, the rate of the reaction (150) is described by the equation[132]

$$\frac{d[Np(VII)]}{dt} = -\frac{d[Np(VI)]}{dt} = k_1[Np(VI)][Fe(CN)_6^{3-}].$$

In a 1.5 M KOH solution (at 10 °C), the ionic strength exerts only a slight effect on the rate constant. Thus the constant k_1 changes from 170 to 215 litre mol^{-1} min^{-1} as μ is increased from 1.5 to 3 (KNO_3). The constant k_1 changes almost directly proportional to the concentration of the hydroxyl ions, *viz*., it increases from 215 to 400 litre mol^{-1} min^{-1} ($\mu = 3$) as the concentration of OH^- is increased from 1.5 to 3 mol litre^{-1}. In a 3 M KOH solution, the activation energy of the reaction (150) is 39 kJ mol^{-1} (10–25 °C).

Neptunium(IV). In a 0.5 M NaOH solution containing a $NpO_2 \cdot n H_2O$ suspension (5.1 mmol litre^{-1}) and $K_3Fe(CN)_6$ (50 mmol litre^{-1}), Np(VI) is formed in less than 15 min.[104] In 6–14 M NaOH solutions, neptunium(VI) is further oxidised to Np(VII).

Plutonium(VI). The reaction of Pu(VI) with $Fe(CN)_6^{3-}$ proceeds at a noticeable rate at [KOH] > 8 mol litre^{-1}.[133] In a 12 M KOH solution containing the ferricyanide ions (2 mmol litre^{-1}), Pu(VI) (0.5 mmol litre^{-1}) is completely oxidised. The reaction rate is high even in the cold. However, the resulting Pu(VII) solutions appeared to be unstable. Apparently, the cyanide ions that are generated upon hydrolysis of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ serve as a reducing agent.

Plutonium(IV). In a 0.2 M NaOH solution containing a suspension of freshly precipitated $PuO_2 \cdot n H_2O$ (1 mmol litre^{-1}), Pu(VI) (0.08 mmol litre^{-1}) was accumulated within 10 min after the addition of $K_3Fe(CN)_6$ (3.3 mmol litre^{-1}). During the same period of time, the concentration of Pu(VI) reached 0.6 and 0.75 mmol litre^{-1} in 1 M and 14 M NaOH solutions, respectively.[104]

Americium(III). In alkaline solutions, Am(III) is oxidised with an excess of the ferricyanide ions to Am(V). This reaction affords the soluble $(AmO_2)_3Fe(CN)_6$ complex, which gradually decomposes to give a precipitate of $Na_2AmO_2(OH)_3 \cdot H_2O$. Hydrated Am(IV) oxide is formed at equal concentrations of Am(III) and $K_3Fe(CN)_6$.[134]

h. Oxidation with CrO_4^{2-} ions

In a 1 M NaOH solution, the potential of the CrO_4^{2-}/CrO_4^{3-} pair is estimated at 0.1 V.[135] Hence, the chromate ions can partially or completely oxidise Np(IV). At room temperature, a suspension of $NpO_2 \cdot n H_2O$ in 0.5–2 M NaOH solutions is slowly oxidised with potassium chromate (the reaction does not proceed to completion during several hours).[104] The resulting Np(V) almost completely remains in the precipitate. The completeness of oxidation is increased as the alkali concentration is increased. In a 14 M NaOH solution, the quantitative transformation of Np(IV) into Np(V) can be achieved already during 1 h. Plutonium(IV) does not react with chromate ions in the range of NaOH concentrations from 0.5 to 14 mol litre^{-1}.[104]

i. Oxidation with MnO_4^- ions

The standard potential of the MnO_4^-/MnO_4^{2-} pair is 0.56 V.[135] The formal potential increases as the ionic strength of the solution is increased. Hence, the MnO_4^- ion must oxidise Np(IV), Np(V), Np(VI) and Pu(IV), Pu(V), Pu(VI).

Neptunium(VI) and plutonium(VI). The reactions of Np(VI) and Pu(VI) with MnO_4^- are reversible[99,136]

$$Np(VI) + MnO_4^- \rightleftharpoons Np(VII) + MnO_4^{2-}, \quad (151)$$

$$Pu(VI) + MnO_4^- \rightleftharpoons Pu(VII) + MnO_4^{2-}, \quad (152)$$

their equilibria are rapidly established at 20–25 °C and depend on the alkali concentration. Neptunium(VI) is oxidised in 3–4 M NaOH solutions but the formation of Np(VII) is generally accompanied by the side reaction, *viz*., gradual reduction of excess MnO_4^- ions with water to MnO_4^{2-}. The potential of the Np(VII)/Np(VI) pair sharply increases as the alkali concentration is decreased, whereas the potential of the MnO_4^-/MnO_4^{2-} pair remains virtually unchanged. Because of this, neptunium(VII) rapidly oxidises MnO_4^{2-} to MnO_4^- in solutions with pH 11.

At high concentrations of alkali, the equilibrium of the reaction involving plutonium is shifted to the right. Plutonium(VI) is oxidised with the MnO_4^- ions only in 10–14 M NaOH solutions.[136] The process is accompanied by the side reaction, *viz*., reduction of excess MnO_4^- ions with water to MnO_4^{2-}. Dilution of alkali to 2–4 mol litre^{-1} leads to rapid oxidation of the manganate ions with plutonium(VII) to MnO_4^-.

Neptunium(IV). In 0.5–1 M NaOH solutions containing a $NpO_2 \cdot n H_2O$ suspension (5 mmol litre^{-1}), neptunium (IV) is oxidised with a fourfold excess of potassium permanganate to Np(VI) during 10 min. Approximately a half amount of Np(VI) remains in the precipitate, whereas the remainder of Np(VI) goes into solution. In 2–14 M NaOH solutions, neptunium passes entirely into solution during the same period of time. At [NaOH] > 6 mol litre^{-1}, Np(VII) was also found in the solution.[104]

Plutonium(IV). In a 0.5 M NaOH solution containing a freshly precipitated suspension of hydrated Pu(IV) oxide (1 mmol litre^{-1}), 10% of dissolved Pu(VI) appears within minutes after the addition of a threefold excess of permanganate ions. The Pu(VI) concentration is not increased with time. An increase in the NaOH concentration is accompanied by an increase in the proportion of dissolved plutonium. In a 14 M NaOH solution, 60% of plutonium is already dissolved.[104]

Americium(III). In alkaline solutions, a suspension of $Am(OH)_3$ is oxidised with the MnO_4^- ions to give hydrated Am(IV) oxide.[123]

j. Oxidation with FeO_4^{2-} ions

In a 1 M NaOH solution, the potential of the Fe(VI)/Fe(III) pair is 0.8 V.[135] This value is higher than the potentials of the Np(V)/Np(IV), Np(VI)/Np(V), Np(VII)/Np(VI) and Pu(V)/Pu(IV), Pu(VI)/Pu(V) pairs in alkaline solutions with the same concentrations. The FeO_4^{2-} ion can oxidise Np(IV) and Pu(IV), but the multielectron transition from Fe(VI) to Fe(III) is accompanied by the structural rearrangement, which is reflected in the rates of the processes.

Neptunium(IV). A suspension (5.1 mmol litre^{-1}) of hydrated Np(IV) oxide in a 0.5 M NaOH solution is slowly oxidised to Np(V) and Np(VI) under the action of a 10-fold excess of K_2FeO_4. An increase in the NaOH concentration is accompanied by acceleration of the process. In a 16 M NaOH solution, neptunium(IV) disappears during several minutes and Np(VII) is formed along with Np(V) and Np(VI).[104]

Plutonium(IV). In the presence of potassium ferrate (20 mmol litre^{-1}), a freshly precipitated suspension of hydrated Pu(IV) oxide in a 0.5 M NaOH solution is slowly dissolved. At $[PuO_2 \cdot n H_2O] = 1$ mmol litre^{-1}, 5.7% of plutonium goes into solution after its storage in the presence of an oxidiser for two days, whereas only 1.5% of plutonium passes into solution in the absence of an oxidiser. In a 14 M NaOH solution, 21% of plutonium goes into solution during the same period of time.[104]

k. Oxidation with XeO_6^{4-} ions

Neptunium(VI). In alkaline solutions, neptunium(VI) is oxidised with the XeO_6^{4-} ions only upon heating. In a 1 M KOH solution (at 70 °C), 50% of Np(VI) is oxidised with the XeO_6^{4-} ions already in 15 min ([Np(VI)] = 0.2 mmol litre^{-1}, $[XeO_6^{4-}] = 1$ mmol litre^{-1}).[129] The reaction rate somewhat increases as the alkali

concentration is decreased. The addition of the perxenate ions to weakly acidic or neutral solutions of Np(VI) does not afford heptavalent neptunium.

Plutonium(VI). In 0–12 M NaOH solutions, plutonium(VI) does not react with the perxenate ions.[119] This is to some extent associated with a decrease in solubility of Na_4XeO_6 in concentrated NaOH solutions. In hot concentrated KOH solutions, plutonium(VI) is partially oxidised with xenon(VIII), but Pu(VII) is formed in low yield.

l. Oxidation with xenon trioxide

In alkaline solutions, xenon trioxide reacts with Np(VI) more actively than the perxenate ions.[129] A 1 M KOH solution containing Np(VI) gradually turns green upon the addition of XeO_3 even in the cold. The reaction proceeds during 3 h. Oxidation of a half amount of neptunium(VI) occurs in a matter of minutes and during ~1 min on heating to 50 and 70 °C, respectively. Oxidation of Np(VI) slows down when the alkali concentration is decreased to 0.25 mol litre^{-1}, whereas an increase in this concentration leads to acceleration of oxidation. In 10–11 M NaOH solutions, Np(VI) (0.2 mmol litre^{-1}) is completely oxidised with a tenfold excess of XeO_3 at 20 °C during 35 min.[74] When Np(VI) and XeO_3 are present in equal concentrations, approximately a half amount of hexavalent neptunium is oxidised during the same period of time.

The reaction of Np(VI) with XeO_3 in alkaline solutions is accompanied by a side process, *viz*., decomposition of the oxidiser to form perxenate, which can also be involved in oxidation of Np(VI).

m. Oxidation with xenon difluoride

Xenon difluoride oxidises Np(VI) only in solutions containing alkali in a moderate concentration.[74, 75] When the reactions are carried out with the use of solid XeF_2, Np(VII) is formed in solutions containing NaOH in a concentration from 0.01 to 1.7 mol litre^{-1}. For achieving quantitative oxidation of Np(VI) in 0.2–1.0 M NaOH or KOH solutions, it is necessary to use a 200-fold excess of solid XeF_2.[75] Aqueous solutions of XeF_2 are more efficient and can oxidise Np(VI) in 5 M KOH solutions. (The reaction proceeds rapidly.[74])

Xenon difluoride can reduce Np(VII). Thus, the addition of XeF_2 (5–200 mg) to a 1 M NaOH solution (20 ml) containing Np(VII) (0.2 mmol litre^{-1}), which was prepared by ozonation, afforded Np(VI) in 3%–12% yields.

The addition of microconcentrations of Co(II) and Ni(II) salts has no noticeable effect on oxidation of Np(VI) with xenon difluoride in a 0.5 M NaOH solution. In the presence of Cu(II) salts (10^{-5} mol litre^{-1}), neptunium(VI) is not oxidised.

When 0.2–1.2 M NaOH solutions of Pu(VI) were treated with a 5–200-fold excess of XeF_2, a colour characteristic of Pu(VII) solutions appeared for only a short period (10 min). Within 3 min after the addition of XeF_2, the yield of Pu(VII) was no higher than 10%.[75] Oxidation of Pu(VI) was not observed in alkaline solutions at a concentration higher than 2 mol litre^{-1}. Upon the addition of XeF_2 to 0.5–3 M KOH or NaOH solutions containing Pu(VII), which was prepared by ozonation, the mixture rapidly turned colourless and the absorption spectra of the solutions were identical with the absorption spectrum of Pu(VI).

n. Oxidation with silver oxides

Neptunium(VI). Neptunium(VII) was prepared in alkaline solutions with the use of Ag_2O and AgO.[93] Oxidation of Np(VI) with silver(I) oxide proceeds at a noticeable rate only in solutions containing alkali in a concentration higher than 8 mol litre^{-1}. At room temperature, the reaction rate was low. It is recommended that the solutions be heated to at least 50 °C. At 60 °C, the process was completed in 15–20 min.

Heating of 9 M and 12 M NaOH solutions containing Np(VI) (0.5 mmol litre^{-1}) and freshly prepared Ag_2O (10 mg ml^{-1}) to 60 °C afforded Np(VII) in 10%–15% and 70%–80% yields, respectively. The yield of Np(VII) was approximately halved as the amount of Ag_2O was decreased from 10 to 2 mg ml^{-1}. The completeness of Np(VI) oxidation was somewhat improved as the temperature was raised to 90 °C.

Oxide AgO oxidised Np(VI) even in a 0.1 M KOH solution. The reaction rate was high even at room temperature. In solutions heated to 50 °C, the reaction equilibrium was established in 3–5 min. In 2–3 M solutions of alkali, an excess of silver(II) oxide oxidised 92%–93% of the total amount of Np(VI).[93]

Plutonium(VI). Silver(II) oxide oxidises Pu(VI) only at an alkali concentration higher than 8 mol litre^{-1}.[136] In an 11 M NaOH solution, the yield of Pu(VII) is close to 100%. In the cold, the reaction rate is low. At 80–90 °C, oxidation of Pu(VI) is completed in less than 15 min.

o. Oxidation with IO_4^- ions, copper(III) periodate and sodium bismuthate

Neptunium(VI) is oxidised with the periodate ions only in hot alkaline solutions.[129] At 85 °C, a half amount of Np(VI) in a 1 M KOH solution containing KIO_4 (0.1 mol litre^{-1}) and Np(VI) (0.2 mmol litre^{-1}) was oxidised during 25 min, whereas the reaction in a 5 M KOH solution was completed in ~10 min.

Plutonium(VI) is not oxidised with the periodate ions both in dilute and concentrated alkaline solutions.[119]

An excess of copper(III) involved in the complex with the periodate ions rapidly oxidises Np(VI) and Pu(VI) in solutions containing NaOH at concentrations higher than 1 and 11 mol litre^{-1}, respectively.[137]

Heterogeneous oxidation of Np(VI) with sodium bismuthate in dilute alkaline solutions proceeds rather rapidly only at the boiling temperature of the solution.[129] The absorption spectra of the green solutions, which are obtained after completion of the reaction and separation of the excess oxidiser by centrifugation, are characteristic of Np(VII).

4. Reduction reactions

a. Reduction with water

Plutonium(VII). The kinetics of reduction of Pu(VII) (0.16–0.25 mmol litre^{-1}) in 0.044–0.1 M KOH solutions is governed by the equation [120]

$$-\frac{d[Pu(VII)]}{dt} = k[Pu(VII)]^{1.2}. \quad (153)$$

The rate constant k decreases as the concentration of the hydroxyl ions is increased. The activation energy of reduction is 60.5 kJ mol^{-1} ($\mu = 1.0$, [KOH] = 0.1 mol litre^{-1}, $T = 25$–45 °C).

It was suggested [120] that the $OH^{\bullet}$ radical is abstracted from the hydrolysed Pu(VII) anion followed by its transformation into the $O^{-}{}^{\bullet}$ radical ion [see the reaction(107)] and then into HO_2^-

$$O^{-}{}^{\bullet} + O^{-}{}^{\bullet} + H_2O \longrightarrow HO_2^- + OH^-. \quad (154)$$

The peroxide ion reduces two Pu(VII) ions.

The rate of reduction of Pu(VII) (1.7 mmol litre^{-1}) in 0.3–1.96 M NaOH solutions obeys the equation [138]

$$-\frac{d[Pu(VII)]}{dt} = k[Pu(VII)]. \quad (155)$$

The apparent rate constant k is proportional to $[OH^-]^n$. Here, $n = 1$ and 2 if $[OH^-] > 1$ mol litre^{-1} and $[OH^-] = 0.3$–0.62 mol litre^{-1}, respectively.

To detect the $OH^{\bullet}$ radicals, which can be generated in this reaction, Pu(VII) was added to 0.5 M and 1.0 M NaOH solutions saturated with benzene. In both cases, the final product of the reaction of $OH^{\bullet}$ with benzene, *viz*., phenol, was not detected. Hence, it was concluded [138] that Pu(VII) involved in the complex $PuO_4(OH)_2^{3-}$ anion eliminates $^1/_2O_2$ and is transformed into Pu(V), which rapidly reacts with Pu(VII). However, no explanation was given as to how one-half of the oxygen molecule was eliminated.

Based on comparison of the standard potentials of the $OH^{\bullet}/OH^-$ (1.9 V) and Pu(VII)/Pu(VI) pairs in a 1 M NaOH solution, it was concluded that one-electron oxidation of OH^- or H_2O with the Pu(VII) ions is thermodynamically impossible. At the same time, the potential of the HO_2^-/OH^- pair in an alkaline medium is 0.867 V.[135] As in the case of Np(VII) reduction in carbonate solutions, the reaction of Pu(VII) with water proceeds through the formation of a dimer.[87,88] It was established that in an alkaline medium Pu(VII) exists as the $PuO_4(OH)_2^{3-}$ anion.[133] A decrease in the alkali concentration leads to the appearance of the $PuO_4(OH)(H_2O)^{2-}$ species, which are dimerised and then decompose into two Pu(VI) ions and H_2O_2 (or HO_2^-).

In a 0.15 M KOH solution, reduction of Pu(VII) is accelerated in the presence of Fe(III), Cu(II), Ni(II) or Co(II) salts.[120] The effect of trivalent iron becomes noticeable starting with the concentration of 7.7×10^{-7} mol litre^{-1}. The rate of Pu(VII) reduction increases proportionally to an increase in the Fe(III) concentration to at least 3.1×10^{-6} mol litre^{-1}. Analogous results were obtained also for Cu(II) and Ni(II). The effect of Co(II) in a 0.15 M KOH solution is manifested at its concentration of $\sim10^{-9}$ mol litre^{-1}. The kinetic curves for Pu(VII) reduction take the shape characteristic of the kinetic curves of autocatalytic reactions. The sensitivity of Pu(VII) to the presence of Co(II) decreases sharply as the OH^- concentration is increased and the curves of Pu(VII) reduction assume the form typical of the kinetic curves of the first-order reactions [as in the case of solutions containing additives of Fe(III), Cu(II) or Ni(II)]. The catalytic action of *d* elements is attributed to their capability for being transformed into higher valence forms, which rapidly react with water.

b. Reduction with hydrogen peroxide

Neptunium(VI) and neptunium (VII).The kinetics of the reactions

$$Np(VI) + HO_2^- \longrightarrow Np(V) + HO_2^{\bullet}, \quad (156)$$

$$Np(VI) + O_2^{-\bullet} \longrightarrow Np(V) + O_2, \quad (157)$$

$$Np(VII) + HO_2^- \longrightarrow Np(VI) + HO_2^{\bullet}, \quad (158)$$

$$Np(VII) + O_2^{-\bullet} \longrightarrow Np(VI) + O_2 \quad (159)$$

in alkaline solutions containing Np(VI) or Np(VII) (0.1 mmol litre^{-1}) at pH 9.2–13.7 was studied by pulse radiolysis.[139] The rate constants for all reactions decrease from 10^4-10^5 to 10^2-10^3 litre mol^{-1} s^{-1} as pH is increased in the above-mentioned range. This is associated with a decrease in the oxidation potentials of the Np(VI)/Np(V) and Np(VII)/Np(VI) pairs.

The kinetics and the mechanism of the reactions of Np(VI) and Np(VII) with H_2O_2 in 1–8.5 M NaOH solutions were examined in the study.[140] It was found that Np(VI) interacts with H_2O_2 to form complexes with 1 : 1 and 1 : 2 compositions. In the latter complex, intramolecular reduction takes place to give the nonequilibrium Np(V)(O_2^{2-}) complex. In the presence of an excess of H_2O_2, the concentration of this complex tends to an equilibrium value. In the presence of an excess of Np(VI), the Np(V)(O_2^{2-}) complex reacts directly with Np(VI). In addition, the complex is decomposed to liberate H_2O_2, which reduces Np(VI).

Hydrogen peroxide reduces Np(VII) to Np(VI) (outer-sphere reduction).

Plutonium(VI) and plutonium(VII). In 1–7 M NaOH solutions (at 23 °C), the stoichiometric coefficient for the reaction of Pu(VI) with H_2O_2 varies from 1.6 to 2.0 and approaches 2 as the $[Pu(VI)]_0/[H_2O_2]$ ratio is increased. The stoichiometry changes only slightly as the temperature is lowered to 10 °C.[141] It can be assumed that the reaction of Pu(VI) with H_2O_2 proceeds according to Eqn (90). At room temperature, the rate of the process in 2–4 M NaOH solutions obeys the equation

$$-\frac{d[Pu(VI)]}{dt} = k[Pu(VI)][H_2O_2], \quad (160)$$

where $k = 5\times10^2$ litre mol^{-1} s^{-1}.

The mechanism of Pu(VI) reduction involves reactions analogous to the reactions (78) and (80), *i.e.*, Pu(VI) forms complexes with hydrogen peroxide. Intramolecular transformations afford Pu(V)

$$Pu(VI) + HO_2^- \longrightarrow complex \longrightarrow Pu(V) + O_2^{-\bullet}. \quad (161)$$

The rate of the reaction of Pu(VI) with H_2O_2 decreases as alkaline solutions of Pu(VI) are aged. For example, the rate constant for the process in a 2 M NaOH solution ([Pu(VI)] = 1 mmol litre^{-1}), which was previously kept for 4 days, decreased to 5 litre mol^{-1} s^{-1}. Probably, this effect is caused by slow polymerisation of Pu(VI).

The reactions of Pu(VII) and Am(VII) with H_2O_2, like those of Np(VII), proceed through an outer-sphere mechanism. In the study,[142] the rate constants for the reactions

$$Pu(VII) + HO_2^- \longrightarrow Pu(VI) + HO_2^{\bullet},$$

$$Am(VII) + HO_2^- \longrightarrow Am(VI) + HO_2^{\bullet},$$

were estimated at $(4-5)\times10^4$ and $(1-4)\times10^6$ litre mol^{-1} s^{-1}, respectively, from the dependence of $\log k$ on the difference between the redox potentials of the An(VII)/An(VI) and HO_2^-/OH^- pairs.

Americium(VI). It is impossible to perform complete oxidation of Am(VI) with ozone because of instability of Am(VII) to reduction with water and also due to side reactions involving ozone.[102] It was expected that an increase in the O_3 concentration in the gaseous phase and solution would lead to acceleration of Am(VI) oxidation, whereas reduction of the resulting Am(VII) with water would be of less importance. However, bubbling of a gaseous mixture with a high ozone content through an alkaline solution of Am(VI) resulted in reduction rather than in oxidation of Am(VI).[143] This is associated with the fact that a large amount of $O_3^{-\bullet}$ radicals was formed due to a high concentration of O_3 and these radicals rapidly decomposed. At a concentration lower than 10^{-5} mol litre^{-1}, the rate of their decomposition is described by the first-order rate equation, whereas this decomposition obeys the rate law for a second-order reaction at a concentration higher than 10^{-5}.[144] In the first case, the reaction affords $O_2^{-\bullet}$, which rapidly reacts with O_3 and, to a small extent, with Am(VI). In the second case, the reaction yields HO_2^-, which reacts rather slowly with O_3 but efficiently reduces Am(VI).

c. Reduction with hydrazine N_2H_4

Neptunium(VII). Neptunium(VII) is rapidly reduced with hydrazine. The examination of the reaction stoichiometry demonstrated [145] that 0.25 g-mol of N_2H_4 were consumed per g-mole of Np(VII)

$$4NpO_4(OH)_2^{3-} + N_2H_4 + 4H_2O \longrightarrow 4NpO_2(OH)_4^{2-} + N_2 + 4OH^-. \quad (162)$$

Neptunium(V). In a 2 M NaOH solution, neptunium(V) (0.2 mmol litre^{-1}) does not react with $N_2H_4\cdot2HCl$ and other hydrazine derivatives, except for $N_2H_4\cdot HNO_3$. The latter reduces Np(V) to Np(IV) at a moderate rate.[146,147] At 20–65 °C, the reaction with $N_2H_4\cdot HNO_3$ (0.1–0.2 mol litre^{-1}) may take from several hours to several days to give a precipitate consisting of Np(IV) and a portion of captured Np(V). Precipitation of neptunium slows down as the NaOH concentration is increased. In a 14 M NaOH solution, the precipitate does not form during the time of the experiment.

Apparently, the starting $N_2H_4\cdot HNO_3$ specimen contains an active compound, which appears after prolonged storage of the reagent at 18–20 °C. For example, HN_3 or $H_2N_2O_2$ can be accumulated in hydrazine. However, these compounds do not reduce Np(V) in an alkaline medium. Hence, the nature of the active compound remains unclear.[147]

In solutions of LiOH containing hydrazine hydrate, Np(V) is not reduced in the temperature range of 40–80 °C. Under the

same condition, the reaction performed in the presence of $PdCl_2$ affords a finely dispersed palladium metal on which hydrated Np(IV) oxide precipitates. The processes are accelerated as the $PdCl_2$ and N_2H_4 concentrations are increased and the temperature is raised, whereas an increase in the alkali concentration from 1 to 5 mol litre^{-1} slows down these processes.[148]

Plutonium(VII). In a 2 M NaOH solution, plutonium(VII) is reduced with hydrazine [119]

$$4\,PuO_4(OH)_2^{3-} + N_2H_4 + 4\,H_2O \longrightarrow$$
$$\longrightarrow 4\,PuO_2(OH)_4^{2-} + N_2 + 4\,OH^-.$$

Plutonium(VI). It was found [149] that in 5–8 M NaOH solutions, $N_2H_4 \cdot HCl$ or $N_2H_4 \cdot HNO_3$ taken in a molar ratio of 1 : 3 with respect to Pu(VI) reduce the latter to Pu(V) in the course of stirring, *i.e.*, the following reactions proceed

$$Pu(VI) + N_2H_4 \longrightarrow Pu(V) + N_2H_3^{\bullet}, \quad (163)$$

$$Pu(VI) + N_2H_3^{\bullet} \longrightarrow Pu(V) + N_2H_2 \quad (164)$$

etc.

Plutonium(V). In 0.5–4 M NaOH solutions, Pu(VI) (0.42 mmol litre^{-1}) is reduced with hydrazine (5 mmol litre^{-1}) to Pu(IV) at 25–55 °C during several minutes.[149] Under these conditions, the reactions (163) and (164) are followed by disproportionation of Pu(V). Accumulation of Pu(IV), while slows down, does not cease as the NaOH concentration is increased (higher than 4 mol litre^{-1}). Under these conditions, disproportionation of Pu(V) may be ignored, *i.e.*, the whole of Pu(IV) is formed as the product of Pu(V) reduction

$$Pu(V) + N_2H_4 \longrightarrow Pu(IV) + N_2H_3^{\bullet}. \quad (165)$$

An increase in the N_2H_4 concentration or temperature leads to acceleration of the Pu(IV) formation. Selective spectrophotometric analysis of dissolved precipitates showed that these precipitates always contain Pu(IV), whereas other valence forms were not detected.

Americium(V). In a 3 M NaOH solution (at 22–23°C), $N_2H_4 \cdot HNO_3$ (10 mmol litre^{-1}) reduces 50% of pentavalent americium (0.2 mmol litre^{-1}) to Am(III) during ~30 h.[150] The process is accelerated as the concentration of hydrazine is increased or the temperature is raised to 50 °C. An increase in the alkali concentration to 6 mol litre^{-1} leads to acceleration of the reaction, whereas a further increase in the alkali concentration slows down this process.

d. Reduction with hydroxylamine

Neptunium(VII). In a 1 M NaOH solution ($T \approx 20$ °C), NH_2OH rapidly reduces Np(VII).[145] The consumption of the reducing agent is 0.75–0.80 mol per mole of Np(VII). Apparently, after the reactions

$$Np(VII) + NH_2OH \longrightarrow Np(VI) + NHOH^{\bullet}, \quad (166)$$

$$Np(VII) + NHOH^{\bullet} \longrightarrow Np(VI) + NOH^{\bullet}, \quad (167)$$

the $NHOH^{\bullet}$ and $NOH^{\bullet}$ radicals are partially consumed in dimerisation reactions.

Neptunium(V). In 0.5–6 M NaOH solutions, NH_2OH (0.5 mol litre^{-1}) reduces Np(V) (0.4 mmol litre^{-1}) at a temperature higher than 60 °C.[146] Efficient reduction occurs at 80–95 °C. When precipitating, the resulting Np(IV) captures a portion of Np(V) from the solution.

Plutonium(VII). The reaction of NH_2OH (without an excess) with Pu(VII) rapidly affords Pu(VI). The reaction stoichiometry is expressed as a fraction,[119] *i.e.*, the process occurs analogously to the reaction of NH_2OH with Np(VII).

Plutonium(VI). In 1–14 M NaOH solutions (at 25–60 °C), NH_2OH (5 mmol litre^{-1}) rapidly reduces Pu(VI) (0.5 mmol litre^{-1}) to Pu(V).[149]

Plutonium(V). In NaOH solutions (at an alkali concentration higher than 4 mol litre^{-1}), hydroxylamine reduces Pu(V) (0.5 mmol litre^{-1}) to Pu(IV) at 25 °C (see Ref. 149)

$$Pu(V) + NH_2OH \longrightarrow Pu(IV) + NHOH^{\bullet}, \quad (168)$$

$$Pu(V) + NHOH^{\bullet} \longrightarrow Pu(IV) + NOH^{\bullet}. \quad (169)$$

The rate of Pu(IV) precipitation and, consequently, of Pu(V) reduction decreases as the NaOH concentration is increased. However, this dependence is not so sharp as that observed in the case of hydrazine. At room temperature, NH_2OH reduces Pu(V) at a moderate rate even in a 14 M NaOH solution. The rate of this process depends substantially on the NH_2OH concentration and temperature.

Americium(V). In a 3 M NaOH solution (at 22–23 °C), hydroxylamine (0.1 mol litre^{-1}) slowly reduces Am(V) (0.2 mmol litre^{-1}) to Am(III).[150] The reaction is accelerated as the NH_2OH concentration is increased, whereas an increase in the alkali concentration slows down this process.

e. Reduction with SO_3^{2-} ions

Neptunium(VII). The kinetics of the reaction of neptunium(VII) with the SO_3^{2-} ions was studied in 0.1–0.5 M NaOH solutions with $\mu = 0.7$ at $T = 20$–35 °C.[145] Under these conditions, Np(VII) is reduced with an excess of sulfite at a moderate rate. The initial regions of the kinetic curves are satisfactorily described by the first-order reaction equation. However, the rate of reduction increases toward the end of the process. This is associated with the fact that Np(VI), which is generated in the course of the process, is reduced with sulfite to Np(V), which reacts with Np(VII) much faster than the sulfite ions. Autocatalytic acceleration of the reaction becomes noticeable when a sufficient amount of Np(VI) is accumulated.

The rate constant for the first-order reaction (k') can be determined from the initial regions of the kinetic curves and then the rate constant k for a bimolecular reaction can be calculated from the $k'/[SO_3^{2-}]$ ratio. The k value is constant in the range of SO_3^{2-} concentrations from 22 to 135 mmol litre^{-1}, *i.e.*, the reaction order with respect to the sulfite ions is equal to unity. The dependence of k on the OH^- concentration

$$k = \frac{k_1}{[OH^-]} + \frac{k_2}{[OH^-]^2}$$

shows that the reaction involves low-charged complex neptunium(VII) anions formed in the processes

$$NpO_4(OH)_2^{3-} + H_2O \rightleftharpoons NpO_4(OH)(H_2O)^{2-} + OH^-, \quad (170)$$

$$NpO_4(OH)_2^{3-} + 2\,H_2O \rightleftharpoons NpO_4(H_2O)_2^- + 2\,OH^-. \quad (171)$$

In a 0.5 M NaOH solution, the activation energy of Np(VII) reduction is 94 kJ mol^{-1}. The reaction with sulfite proceeds as follows:

$$Np(VII) + SO_3^{2-} \longrightarrow Np(VI) + SO_3^{-\bullet}, \quad (172)$$

$$Np(VII) + SO_3^{-\bullet} \longrightarrow Np(VI) + SO_3(SO_4^{2-}), \quad (173)$$

$$Np(VI) + SO_3^{2-} \longrightarrow Np(V) + SO_3^{-\bullet} \quad (174)$$

and is accompanied by reproportionation [see the reaction (94)].

The process of Np(VII) reduction with sulfite ions is affected by impurities of Cu(II), Co(II) and Mn(VII) compounds. The catalytic action of copper(II) becomes noticeable at its concentration of 2×10^{-7} mol litre^{-1}.[145] The rate constant for the reaction linearly increases as the $CuCl_2$ concentration is increased from 5×10^{-7} to $\sim 5 \times 10^{-6}$ mol litre^{-1}

$$k = k^0 + k'[Cu(II)], \quad (175)$$

where k^0 is the rate constant for the reaction in the absence of a catalyst, $k' = 1.4 \times 10^6$ litre^2 mol^{-2} min^{-1} at $\mu = 0.7$ and

$T = 25$ °C. Cobalt(II) and manganese(II) are similar in catalytic activity to copper(II).

In addition to the above-mentioned metal ions, iron(III) also serves as a catalyst of this reaction but the concentration of the latter must be no lower than 10^{-5} mol litre^{-1}. Silver(I) compounds have no effect on the rate of Np(VII) reduction with the SO_3^{2-} ions.

Neptunium(V). At a concentration of 5 mmol litre^{-1}, the sulfite ions have no effect on Np(V).[146] High concentrations of sulfite are required for reduction of Np(V) in 3–5 M NaOH solutions at 20 °C. However, Np(V) (0.2 mmol litre^{-1}) is reduced only by 15% during 24 h even at $[SO_3^{2-}] = 1$ mol litre^{-1}.[151]

Plutonium(VII) and plutonium(V). In 1.2–2.5 M KOH solutions ($T = 25$ °C), Pu(VII) is rapidly reduced with the SO_3^{2-} ions.[152] In a 4 M NaOH solution, plutonium(V) does not react with sulfite ions at a concentration of 0.1 mol litre^{-1}.[149]

Americium(V). The SO_3^{2-} ions slowly reduce Am(V). In a 1.5 M NaOH solution containing Am(V) (0.23 mmol litre^{-1}) and Na_2SO_3 (0.11 mol litre^{-1}), a half amount of Am(V) is reduced at 22–23 °C during 9 h.[150] The reaction is accelerated as the sulfite concentration is increased.

f. Reduction with $S_2O_3^{2-}$ ions

Neptunium(VII) and neptunium(V). The thiosulfate ion acts as a weak reducing agent with respect to Np(VII) and Np(V). In a 2 M NaOH solution containing $Na_2S_2O_3$ (0.05 mol litre^{-1}), a half amount of Np(VII) is reduced at 25°C in a time longer than 100 min,[145] whereas Np(V) is reduced only by 18% even under the action of $Na_2S_2O_3$ (1 mol litre^{-1}) during 24 h.[151] Heating or a decrease in the NaOH concentration to 0.1 mol litre^{-1} leads to a slight acceleration of Np(VII) reduction.[145]

Plutonium(VII). The reaction of Pu(VII) with the thiosulfate ions proceeds at a moderate rate. The time of reduction of a half amount of Pu(VII) (0.5 mmol litre^{-1}) in a 2.5 M KOH solution containing $Na_2S_2O_3$ (2.5 mmol litre^{-1}) is 2 min. The reaction rate increases as the concentration of the reducing agent is increased.[152]

g. Reduction with $S_2O_4^{2-}$ ions and thiourea dioxide

The dithionite ions and thiourea dioxide also reduce Np(V), Pu(V) and Am(V). In a 4 M NaOH solution, dithionite (0.1 mol litre^{-1}) reduces only 30% of neptunium(V) (0.4 mmol litre^{-1}) at 20°C during one day. In the presence of $(NH_2)_2CSO_2$ (0.1 mol litre^{-1}), 20% of Np(V) is reduced at 65 °C for 3 h.[146]

In a 4 M NaOH solution containing $S_2O_4^{2-}$ (5 mmol litre^{-1}), 90% of plutonium(V) (0.4 mmol litre^{-1}) precipitates at 50 °C for 20 min. In the presence of thiourea dioxide (5 mmol litre^{-1}), the same amount of plutonium precipitates during 2 min.[149] The Pu(IV) and Pu(V) contents in the precipitate are unknown.

In a 1.5 M NaOH solution containing dithionite (5 mmol litre^{-1}), 50% of Am(V) (0.23 mmol litre^{-1}) is reduced at 22–23 °C for 5 h. In the presence of $(NH_2)_2CSO_2$ (0.1 mol litre^{-1}), the same amount of Am(V) is reduced during 0.2 h. Reduction is accelerated as the concentrations of the reagents are increased.[150]

h. Reduction with iodide ions

Neptunium(VII). The iodide ions (90–160 mmol litre^{-1}) reduce Np(VII) at a moderate rate without heating at $[OH^-] <$ 0.03 mol litre^{-1}.[145] The reaction of Np(VII) directly with I^- proceeds rather slowly. The reaction is accelerated as oxidation products of iodide ions are accumulated in solution. The addition of a mixture of I_2 and KI, *i.e.*, the I_3^- ions, to the reaction mixture exerts an even stronger effect. The presence of Np(VI) has no effect on the reaction. Reduction of Np(VII) is accelerated as the I^- concentration is increased or the alkali concentration is decreased. The process involves the reactions

$$\mathrm{Np(VII)} + \mathrm{I^-} \xrightarrow{\text{very slow}} \mathrm{Np(VI)} + \mathrm{I}, \tag{176}$$

$$\mathrm{I^-} + \mathrm{I} \xrightarrow{\text{fast}} \mathrm{I_2^-}, \tag{177}$$

$$\mathrm{Np(VII)} + \mathrm{I_2^-} \xrightarrow{\text{fast}} \mathrm{Np(VI)} + \mathrm{I_2}, \tag{178}$$

$$\mathrm{I^-} + \mathrm{I_2} \xrightarrow{\text{fast}} \mathrm{I_3^-}, \tag{179}$$

$$\mathrm{I_2} + 2\,\mathrm{OH^-} \longrightarrow \mathrm{IO^-} + \mathrm{I^-} + \mathrm{H_2O}, \tag{180}$$

$$\mathrm{Np(VII)} + \mathrm{I_3^-} \xrightarrow{\text{slow}} \mathrm{Np(VI)} + \mathrm{I_2} + \mathrm{I}. \tag{181}$$

The possibility of the reaction of Np(VII) with IO^- was not examined.

The addition of microamounts of Co(II), Cu(II) or Mn(II) leads to acceleration of Np(VII) reduction with the I^- ions. The catalytic effect becomes noticeable when these metals are present in concentrations of $(1-2) \times 10^7$ mol litre^{-1}.

Plutonium(VII). In KOH solutions, plutonium(VII) is reduced with equimolar amounts of KI at a high rate even at room temperature.[152] The reaction proceeds to completion even if the concentration of the reducing agent is 7–8 times lower than the concentration of Pu(VII). Consequently, all intermediate products of oxidation of I^- to IO_4^- (or $H_3IO_6^{2-}$) react with Pu(VII) due to the high potential of the Pu(VII)/Pu(VI) pair. The possibility of Pu(VII) reduction with the IO^- and IO_3^- ions was confirmed experimentally. Hence, the reaction of Pu(VII) with insufficient I^- proceeds according to the equation

$$8\,\mathrm{Pu(VII)} + \mathrm{I^-} \longrightarrow 8\mathrm{Pu(VI)} + \mathrm{I(VII)}. \tag{182}$$

In the presence of an excess of the reducing agent, the character of the reaction depends substantially on the alkali concentration. At [KOH] < 2 mol litre^{-1}, the rate of Pu(VII) reduction is described by the equation

$$-\frac{\mathrm{d[Pu(VII)]}}{\mathrm{d}t} = k[\mathrm{Pu(VII)}][\mathrm{I^-}]. \tag{183}$$

In a 1 M KOH solution (at 25 °C), the constant k is 6.5×10^3 litre mol^{-1} min^{-1}. The constant k decreases by a factor of ~ 50 as the alkali concentration is increased to 3.3 mol litre^{-1}. For a 2.5 M KOH solution, the temperature dependence of k in the range of 25–53 °C corresponds to the apparent activation energy of 25 kJ mol^{-1}. Reduction of Pu(VII) begins with the reaction

$$\mathrm{Pu(VII)} + \mathrm{I^-} \xrightarrow{\text{slow}} \mathrm{Pu(VI)} + \mathrm{I}, \tag{184}$$

followed by the reaction (177)

$$\mathrm{Pu(VII)} + \mathrm{I_2^-} \xrightarrow{\text{fast}} \mathrm{Pu(VI)} + \mathrm{I_2}. \tag{185}$$

and then the reactions (179) and (180) take place.

The kinetic curves for Pu(VII) reduction with an excess of KI in solutions with [KOH] > 2 mol litre^{-1} are distorted, the distortion being stronger at higher alkali concentrations. For 4 M KOH solutions, the curves assume an S shape, which was attributed [152] to the fact that intermediate products of I^- oxidation to I(VII) are involved in Pu(VII) reduction to an increasing extent. In our opinion, under these conditions I_2^- reduces Pu(VI) to Pu(V), which rapidly reacts with Pu(VII).

i. Reduction with iodate ions

Plutonium(VII). In 0.5–3.5 M KOH solutions (at 15–35 °C), reduction of Pu(VII) with iodate ions proceeds irreversibly according to the stoichiometric equation [152]

$$2\,\mathrm{Pu(VII)} + \mathrm{IO_3^-} = 2\,\mathrm{Pu(VI)} + \mathrm{I(VII)}. \tag{186}$$

The rate of the process is governed by the equation

$$-\frac{\mathrm{d[Pu(VII)]}}{\mathrm{d}t} = k[\mathrm{Pu(VII)}][\mathrm{IO_3^-}]. \tag{187}$$

In a 1 M KOH solution (at 25 °C), the rate constant for the reaction (186) is 1.1×10^3 litre mol^{-1} min^{-1}. As the alkali concentration of increased from 0.17 to 1.7 mol litre^{-1}, the constant k decreases in an inverse proportion to [OH$^-$] and then remains virtually unchanged up to [KOH] = 3.5 mol litre^{-1}.

An increase in the temperature leads to a rather small increase in the rate of Pu(VII) reduction. In a 2.5 M KOH solution, the apparent activation energy is 24 kJ mol^{-1}.

The mechanism of Pu(VII) reduction with the iodate ions can be described by the following scheme:

$$Pu(VII) + I(V)O_3^- \longrightarrow Pu(VI) + I(VI), \quad (188)$$

$$Pu(VII) + I(VI) \longrightarrow Pu(VI) + I(VII). \quad (189)$$

j. Reduction with $Fe(CN)_6^{4-}$, tin(II) and vanadium(IV) ions

The $Fe(CN)_6^{4-}$ ions rapidly reduce Np(VII) in a 1 M NaOH solution[145] [the equilibrium of the reaction (150) is shifted to the left] and Pu(VII) in a 5 M NaOH solution.[119] According to our estimation, the equilibrium constant of the reaction (150) in a 1.5 M KOH solution is 0.1 ($T = 23$ °C). We estimated the rate constant for oxidation [the equilibrium of the reaction (150) is shifted to the right] as 350 litre mol^{-1} min^{-1} in going from 10 to 23 °C. The rate constant for reduction was estimated at 3500 litre mol^{-1} min^{-1}.

Tin(II) reduces Np(VII) in a 1 M NaOH solution[145] and Pu(VII) in 1.5–2.5 M NaOH solutions in the course of stirring.[152]

At 20–80 °C, vanadium(IV) (20 mmol $litre^{-1}$) reduces Np(V) (0.2 mmol $litre^{-1}$) in 1–5 M NaOH solutions as a result of which Np(IV) precipitates and captures a portion of Np(V) from the solution.[153] Reduction slows down as the alkali concentration is increased and is accelerated as the temperature is raised.

k. Reduction with organic compounds

Neptunium(VII). The ascorbate ions rapidly reduce Np(VII).[145] The semiquantitative data on reduction of Np(VII) with other organic compounds are given in Table 4.

At 25 °C, Np(VII) does not virtually react with ethanol, acetate ions and oxalate ions both in 2 M and 0.1 M alkaline solutions. The resistance of Np(VII) to ethanol and oxalate ions is decreased (particularly, at a low concentration of the OH^- ions) when the temperature is raised to 65 °C. Formaldehyde rapidly reduces Np(VII) under all conditions being studied, whereas the other compounds react with Np(VII) at a moderate rate.

The kinetics of the reactions of Np(VII) with aliphatic alcohols, formaldehyde and formate ions in alkaline solutions was examined in the studies.[154–159] For all systems, the reaction rate is governed by the equation

$$-\frac{d[Np(VII)]}{dt} = k[Np(VII)] = k_0[Red]^n[OH^-]^m[Np(VII)],$$

where k_0 is the rate constant at [Red] = 1 mol $litre^{-1}$, [OH^-] = 1 mol $litre^{-1}$, $T = 25$ °C. The kinetic parameters are given in Table 5.

Table 4. Time of reduction of a half amount of Np(VII) ($\tau_{1/2}$) with organic compounds.[145]

Reducing agent (Red)	[Red][a]	$\tau_{1/2}$ /min			
		[OH^-] = 0.1 mol $litre^{-1}$		[OH^-] = 2 mol $litre^{-1}$	
		25 °C	65 °C	25 °C	65 °C
Oxalate ion	0.070	> 100	32	> 100	> 100
Acetate ion	0.200	> 100	> 100	> 100	> 100
EDTA	0.010	75	1.1	> 100	45
Citrate ion	0.090	12	0.4	–	22
Formate ion	0.090	50	2.5	> 100	20
Ethanol	1.500	> 100	5	> 100	30
Formaldehyde	0.060	1.5	0.1	–	0.3

[a] In mol $litre^{-1}$.

Analysis of the data from Table 5 shows that the rate constant for oxidation decreases as the number of atoms in normal alcohols is increased. Oxidation products of alcohols are more reactive than alcohols as such.

Neptunium(V). In 1–5 M NaOH solutions containing up to 1 mol $litre^{-1}$ of HCOONa, Np(V) is not reduced at 60–90 °C during 5 h. Under the same conditions, the reactions performed in the presence of palladium salts afford palladium metal on which hydrated Np(IV) oxide precipitates. Platinum salts also exert a catalytic effect on Np(V) reduction, although this process is less efficient than that occurring in the presence of palladium salts. Reduction of neptunium(V) with the formate ions proceeds on its contact with an anion-exchange resin covered with palladium or platinum metal.[161]

Plutonium(VII). The ascorbate ions rapidly reduce Pu(VII).[152] The semiquantitative data on the reactions with some other compounds, which react with Pu(VII) more slowly, are presented in Table 5.

It can be seen that the reaction of Pu(VII) with ethanol is less efficient than that with methanol and the rate constants for Pu(VII) reduction with these alcohols are much higher than the analogous constants for Np(VII).

Table 5. Effect of the nature of the reducing agent (Red) and the reaction conditions on stability of Np(VII) and Pu(VII).

Red	[Red] /mol $litre^{-1}$	[KOH] /mol $litre^{-1}$	T /°C	$10^2 k$ /min^{-1}	n	m	E_a /kJ mol^{-1}	$10^4 k_0$	Ref.
Data for Np(VII)									
CH_3OH	16.4	1.0	28.2	3.84	0.74	−1.5	50.7 ± 3.4	44.0	154
C_2H_5OH	3.4	1.0	38.9	0.69	1.5	−1.1	49.7 ± 2.6	4.47	154
n-C_3H_7OH	0.28	1.0	60.4	0.80	0.9	−0.96	46.3 ± 3.0	34.5	155
n-C_4H_9OH	0.22	1.0	60.4	0.28	0.6	−1.0	58.4 ± 3.6	5.77	156
n-$C_5H_{11}OH$	0.10	1.0	60.4	0.14	0.8	−1.0	81.4 ± 4.5	2.71	156
iso-C_3H_7OH	0.26	1.0	55.6	0.37	0.8	−1.0	52.0 ± 2.0	16.4	157
iso-C_4H_9OH	0.22	1.0	55.6	0.23	0.8	−1.0	54.0 ± 2.0	10.9	157
iso-$C_5H_{11}OH$	0.11	0.5	60.4	0.40	1.0	−0.95	71.0 ± 3.0	9.0	155
CH_2O	0.0075	1.0	29.6	1.23	1.0	−1.0	59.0 ± 4.0	1.14×10^4	158
$(CH_3)_2CO$	0.27	1.0	30.3	0.42	0.9	−1.0	49.0 ± 2.0	96.0	158
HCOONa	0.01	0.2[a]	65.0	1.45	0.6	−0.33	56.0 ± 2.0	93.0	159
Data for Pu(VII)									
CH_3OH	0.55	2.5	25.0	60.3	–	–	–	–	152
	0.034	0.95[a]	25.2	0.26	1.5	−0.3	50.0 ± 4.0	4×10^3	160
CH_2O	0.004	2.5	25.0	55.5	–	–	–	–	152
C_2H_5OH	0.55	2.5	25.0	39.6	–	–	–	–	152
	0.024	0.94[a]	25.2	0.23	0.9	−0.8	44.0 ± 4.0	6.3×10^2	160

[a] NaOH was used as the medium.

l. Reduction with metals

Reduction of Np(VII), Pu(VI) and Am(VI) in alkaline solutions with aluminium metal was examined in the study.[162] The reactions were carried out at room temperature. A 2–6 cm^2 aluminium plate was submerged in an alkaline solution of actinide, which was vigorously stirred. Reduction of neptunium(VII) (0.1–2 mmol · $litre^{-1}$) in a 0.1–2 M NaOH solution was completed in 8–20 min depending on the alkali concentration and the size of the plate. Neptunium (25%–50%) partially precipitated on the aluminium plate as a thin layer, which was firmly attached to the support. The precipitate contained only Np(V). Reduction of Pu(VI) was completed in 5–20 min to give a colloid of Pu(IV) and a precipitate of hydrated Pu(IV) oxide; 5–7 μg cm^{-2} of plutonium precipitated on the aluminium surface. The amount of the precipitate varied with the concentrations of plutonium and alkali.

A precipitate of Am(III) hydroxide rapidly formed upon reduction of Am(VI). The amount of americium precipitated on the aluminium surface was no higher than 6 μg cm^{-2}.

The reactions of Np(V) and Pu(VI) with zinc, chromium, tin and their alloys in 0.5–4 M NaOH solutions were examined under static and dynamic conditions (filtration of solutions through a column filled with metal granules).[163] Reduction of actinides and precipitation of hydroxides took place on the surface of metallic granules. In the case of plutonium, the best result was achieved on contact of chromium granules with a solution of Pu(VI) in 0.5 M NaOH at 60 °C for 2–5 h. The best sorption of neptunium from a 1 M NaOH solution was attained upon prolonged contact with chromium and zinc granules.

An increase in the alkali concentration and the addition of chromate ions and complex-forming agents slow down sorption of plutonium.

V. Conclusion

Abundant data were accumulated on redox reactions of actinides in carbonate and alkaline solutions. Procedures for oxidation of low-valence forms of neptunium, plutonium and americium and stability of high-valence forms of these elements were studied in detail. In many cases, the transitions between the oxidation states V, VI and VII proceed easily because they do not require substantial structural rearrangements of the ions. By contrast, the transition IV → V giving rise to an 'yl' group proceeds slowly. The proposed mechanisms of redox processes are consistent with the concepts of general chemistry. However, many of these mechanisms call for experimental or quantum-chemical verification.

Among the reactions to be studied, the following reactions, in our opinion, are of most interest: disproportionation of Pu(V) in a wide range of concentrations of bicarbonate and carbonate ions; the reactions of Np(IV), Pu(IV) and Am(IV) with ozone in carbonate solutions; oxidation of Np(V) and Pu(V) with ferricyanide ions in concentrated carbonate solutions; reactions of Np(VI) and Pu(VI) with hydrogen peroxide in bicarbonate-carbonate solutions; and disproportionation of Pu(VI) in concentrated alkaline solutions (if this process does not occur, it is necessary to establish the causes).

Problems of the preparation of macroamounts of curium(VI) (attempts to solve this problem were unsuccessful [164]) and Pu(VIII) are of particular interest. It was suggested [165] that Pu(VIII) can be produced upon β decay of ^{239}Np(VII) in the solid state

$$^{239}NpO_6^{5-} \longrightarrow {}^{239}PuO_6^{4-}.$$

In this connection, the fundamental question arises as to the form of existence of Pu(VIII) and its stability. The estimated potential of the Pu(VIII)/Pu(VII) pair is higher than 3 V,[166] which excludes the existence of Pu(VIII) in solution or the gaseous phase. However, it was reported [167, 168] that plutonium was oxidised with molecular oxygen to PuO_4 under the conditions of gas thermochromatography. This compound is comparable in volatility to octavalent osmium oxide (OsO_4). Undoubtedly, there is a need to carry out further experiments on the determination of the composition of the volatile plutonium compound, including studies with the use of modern methods of analysis, which allow one to determine the structures and compositions of specimens with a weight of several nanograms (in particular with the use of X-ray synchrotron radiation).[169]

References

1. D L Clark, D E Hobart, M P Neu *Chem.Rev.* **95** 25 (1995)
2. V F Peretrukhin, V P Shilov, A K Pikaev *Alkaline Chemistry of Transuranium Elements and Technetium and the Treatment of Alkaline Radioactive Wastes (Report WHC-EP-0817 UC-601)* (Richland, Washington, DC: Westinghouse Hanford Co., 1995)
3. A K Pikaev, V P Shilov, A V Gogolev *Usp. Khim.* **66** 845 (1997) [*Russ. Chem. Rev.* **66** 763 (1997)]
4. A B Yusov, V P Shilov *Izv. Akad. Nauk, Ser. Khim.* 1957 (2000) [a]
5. D W Wester, J C Sullivan *Inorg. Chem.* **19** 2838 (1980)
6. W A Mulac, S Gordon, K N Schmidt, D Wester, J C Sullivan *Inorg. Chem.* **23** 1639 (1984)
7. E Haltier, B Fourest, F David *Radiochim. Acta* **51** 107 (1990)
8. A M Fedoseev, V F Peretrukhin, N N Krot *Dokl. Akad. Nauk SSSR* **244** 1187 (1979) [b]
9. C Musicas, G Rousset *Note CEA* **1419** 431 (1971)
10. J J Katz, G T Seaborg, L Morss (Eds), in *The Chemistry of Actinide Elements* Vol. 2 (London; New York: Chapman and Hall, 1986) p. 1143
11. D W Wester, J C Sullivan *J. Inorg. Nucl. Chem.* **43** 2919 (1981)
12. P G Varlashkin, D E Hobart, G M Begun, J R Peterson *Radiochim. Acta* **35** 91 (1984)
13. G A Simakin, Yu F Volkov, G I Visyashcheva, I I Kapshukov, P F Baklanova, G N Yakovlev *Radiokhimiya* **16** 859 (1974) [c]
14. A J Zielen, D Cohen *J. Phys. Chem.* **74** 394 (1970)
15. G A Simakin, I V Matyashchuk, N A Vladimirova *Radiokhimiya* **15** 98 (1973) [c]
16. V P Shilov, N N Krot, A D Gel'man *Radiokhimiya,* **12** 697 (1970) [c]
17. V F Peretrukhin, D P Alekseeva *Radiokhimiya* **16** 836 (1974) [c]
18. V P Shilov, A B Yusov *Radiokhimiya* **39** 503 (1997) [c]
19. V F Peretrukhin, V I Spitsyn *Izv. Akad. Nauk SSSR, Ser. Khim.* **4** 826 (1982) [a]
20. V F Peretrukhin, N N Krot, A D Gel'man *Radiokhimiya* **14** 72 (1972) [c]
21. V S Ermakov, V F Peretrukhin, N N Krot *Radiokhimiya* **19** 324 (1977) [c]
22. V S Ermakov, V F Peretrukhin, N N Krot *Radiokhimiya* **19** 253 (1977) [c]
23. D W Wester, J C Sullivan *Radiochem. Radioanal. Lett.* **57** 35 (1983)
24. P G Varlashkin, G M Begun, J R Peterson *Radiochim. Acta* **35** 211 (1984)
25. J Bourges *Radiochem. Radioanal. Lett.* **12** 111 (1972)
26. V F Peretrukhin, D P Alekseeva *Radiokhimiya* **16** 843 (1974) [c]
27. N A Bubantseva, I G Tananaev, A M Fedoseev, C H Delegard *J. Alloys. Comp.* **271–273** 813 (1998)
28. V P Shilov *Radiokhimiya* **18** 688 (1976) [c]
29. G A Simakin *Radiokhimiya* **19** 518 (1977) [c]
30. J Y Bourges, B Guillaume, G Koehly, D E Hobart, J R Peterson *Inorg. Chem.* **22** 1179 (1983)
31. D E Hobart, K Samhoun, J R Peterson *Radiochim. Acta.* **31** 139 (1982)
32. V Ya Frenkel', I A Lebedev, P L Khizhnyak, B F Myasoedov *Radiokhimiya* **27** 405 (1985) [c]
33. V Ya Frenkel', I A Lebedev, P L Khizhnyak, B F Myasoedov *Radiokhimiya* **27** 576 (1985) [c]
34. P Berger, P Blank, J Bourges *Radiochim. Acta* **43** 217 (1988)
35. V B Nikolaevskii, V P Shilov, N N Krot, V F Peretrukhin *Radiokhimiya* **17** 426 (1975) [c]
36. V B Nikolaevskii, V P Shilov, N N Krot *Radiokhimiya* **16** 122 (1974) [c]
37. V F Peretrukhin, V B Nikolaevskii, V P Shilov *Radiokhimiya* **16** 833 (1974) [c]
38. L L Borin, A I Karelin *Termodinamika Okislitel'no-Vosstanovitel'nykh Protsessov v Tekhnologii Aktinidov* (Thermodynamics of

Redox Processes in the Technology of Actinides) (Moscow: Atomizdat, 1977)
39. M Voković, D Cukman, V Pravdić *J. Electroanal. Chem.* **54** 209 (1974)
40. V P Shilov, A V Gogolev, A K Pikaev *Dokl. Akad. Nauk* **375** 362 (2000) [b]
41. V P Shilov, A B Yusov *Radiokhimiya* **35** (5) 61 (1993) [c]
42. L M Frolova, V M Chistyakov, V M Ermakov, A G Rykov *Radiokhimiya* **18** 281 (1976) [c]
43. V M Chistyakov, V M Ermakov, A G Rykov *Radiokhimiya* **16** 553 (1974) [c]
44. V P Shilov, A B Yusov *Radiokhimiya* **37** 201 (1995) [c]
45. V P Shilov, E S Stepanova, N N Krot *Radiokhimiya* **18** 350 (1976) [c]
46. V P Shilov, A B Yusov *Radiokhimiya* **37** 203 (1995) [c]
47. V P Shilov, L N Astafurova, A B Yusov *Radiokhimiya* **37** 507 (1995) [c]
48. E A Kanevskii, I V Goncharov, V B Rengevich *Radiokhimiya* **7** 579 (1965) [c]
49. V Hirsch, K H Lieser *Radiochim. Acta* **44**/**45** Pt 1 7 (1988)
50. A P Filippov, V N Fedoruk *Radiokhimiya* **32** (1) 15 (1990) [c]
51. J S Coleman, T K Keenan, L N Jones, W T Carnall, R A Penneman *Inorg. Chem.* **2** 58 (1963)
52. S W Rabideau, B J Masters *J. Phys. Chem.* **67** 318 (1963)
53. G Gordon, H Taube *Inorg. Chem.* **1** 69 (1962)
54. A R Felmy, D Rai, R W Fulton *Radiochim. Acta* **50** 193 (1992)
55. C Keller, D Fang *Radiochim. Acta* **11** 123 (1969)
56. L M Frolova, V M Chistyakov, V M Ermakov, A G Rykov *Radiokhimiya* **17** 410 (1975) [c]
57. I M Kolthoff, I K Miller *J. Am. Chem. Soc.* **73** 3055 (1951)
58. L M Frolova, V M Chistyakov, V M Ermakov, A G Rykov *Radiokhimiya* **18** 276 (1976) [c]
59. V P Shilov, L N Astafurova, A B Yusov *Radiokhimiya* **37** 509 (1995) [c]
60. V P Shilov, N N Gavrilova *Radiokhimiya* **22** 603 (1980) [c]
61. P Neta, R E Huie *J. Phys. Chem. Ref. Data* **17** 1027 (1988)
62. A V Gogolev, V P Shilov, A K Pikaev *Izv. Akad. Nauk SSSR, Ser. Khim.* 20 (1989) [a]
63. M P Mefod'eva, N N Krot, A D Gel'man, T V Afonas'eva *Radiokhimiya* **18** 93 (1976) [c]
64. V M Ermakov, V M Chistyakov, L M Frolova, A G Rykov *Radiokhimiya* **19** 234 (1977) [c]
65. V M Ermakov, A G Rykov, G A Timofeev, Ashok V Dzhadov, G N Yakovlev *Radiokhimiya* **15** 380 (1973) [c]
66. V M Chistyakov, V M Ermakov, A D Mokrousov, A G Rykov *Radiokhimiya* **16** 810 (1974) [c]
67. A V Gogolev, V P Shilov, A M Fedoseev, A K Pikaev *Izv. Akad. Nauk SSSR, Ser. Khim.* **1** 28 (1990) [a]
68. A K Pikaev, V P Shilov, V I Spitsyn *Dokl. Akad. Nauk SSSR* **232** 387 (1977) [b]
69. P L Khizhnyak, Author's Abstracts of Candidate Thesis in Chemical Sciences, V I Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences of the USSR, Moscow, 1987
70. G T Seaborg, J J Katz (Eds) *The Actinide Elements* (New York; Toronto; London: McGraw-Hill, 1954)
71. A B Yusov, A V Anan'ev, V P Shilov *Izv. Akad. Nauk, Ser. Khim.* 953 (1994) [a]
72. V P Shilov, A B Yusov *Radiokhimiya* **36** 396 (1994) [c]
73. A V Anan'ev, V P Shilov, A B Yusov *Radiokhimiya* **36** 247 (1994) [c]
74. V D Klimov, V N Prussakov, V B Sokolov *Radiokhimiya* **13** 725 (1971) [c]
75. Yu K Gusev, V F Peretrukhin, V P Shilov, N S Kirin *Radiokhimiya* **14** 888 (1972) [c]
76. E H Appelman *Inorg. Chem.* **6** 1305 (1967)
77. E H Appelman *Inorg. Chem.* **10** 1881 (1971)
78. A A Goncharov, Yu N Kozlov, A P Purmal' *Zh. Fiz. Khim.* **55** 1633 (1981) [d]
79. E H Appelman, J G Malm *J. Am. Chem. Soc.* **86** 2141 (1964)
80. A B Yusov, V P Shilov *Radiokhimiya* **34** (6) 31 (1992) [c]
81. V P Shilov, A B Yusov *Radiokhimiya* **35** (1) 38 (1993) [c]
82. A B Yusov, V P Shilov *Radiokhimiya* **35** (2) 38 (1993) [c]
83. U K Kläning, K Sehested, T Wolff, E H Appelman *J. Chem. Soc., Faraday Trans. 1* 1539 (1982)
84. P A G O'Hare, G K Johnson, E H Appelman *Inorg. Chem.* **9** 332 (1970)
85. V F Peretrukhin, E A Erin, V I Dzyubenko, V V Kopytov, V G Polyukhov, V Ya Vasil'ev, G A Timofeev, A G Rykov, N N Krot, V I Spitsyn *Dokl. Akad. Nauk SSSR* **242** 1359 (1978) [b]
86. V N Kosyakov, E A Erin, V M Vityutnev, V V Kopytov, A G Rykov *Radiokhimiya* **24** 551 (1982) [c]
87. V P Shilov *Zh. Fiz. Khim.* **70** 1915 (1996) [d]
88. V P Shilov, A B Yusov *Radiokhimiya* **41** 416 (1999) [c]
89. K Nash, M E Noon, S Fried, J C Sullivan *Inorg. Nucl. Chem. Lett.* **16** 33 (1980)
90. J C Sullivan, W Brown, K Nash, M Thompson *Radiochim. Acta* **30** 45 (1982)
91. J Beitz, C Johan, J C Sullivan, M Woods *Radiochim. Acta* **40** 7 (1986)
92. C J Anderson, M Woods, E Deutsch, K Deutsch, J C Sullivan *Radiochim. Acta* **61** 137 (1993)
93. N N Krot, M P Mefod'eva, V P Shilov, A D Gel'man *Radiokhimiya* **12** 471 (1970) [c]
94. V S Ermakov, T N Bukhtiyarova, N N Krot *Radiokhimiya* **19** 250 (1977) [c]
95. I G Tananaev *Radiokhimiya* **32** (1) 20 (1990) [c]
96. V B Nikolaevskii, V P Shilov, N N Krot, V F Peretrukhin *Radiokhimiya* **17** 431 (1975) [c]
97. V P Shilov *Radiokhimiya* **39** 330 (1997) [c]
98. A K Pikaev, V P Shilov *Izv. Akad. Nauk SSSR, Ser. Khim.* **9** 2136 (1978) [a]
99. V P Shilov, N N Krot, A D Gel'man *Radiokhimiya* **12** 911 (1970) [c]
100. C W Williams, J-P Blaudeau, J C Sullivan, M R Antonio, B Bursten, L Soderholm *J. Am. Chem. Soc.* **123** 4346 (2001)
101. N N Krot, V P Shilov, V B Nikolaevskii, A K Pikaev, A D Gel'man, V I Spitsyn *Dokl. Akad. Nauk SSSR* **217** 589 (1974) [b]
102. V P Shilov *Radiokhimiya* **18** 659 (1976) [c]
103. N A Budantseva, V P Shilov, N N Krot *Radiokhimiya* **40** 544 (1998) [c]
104. V P Shilov, L N Astafurova, A Yu Garnov, A B Yusov, N N Krot *Radiokhimiya* **39** 437 (1997) [c]
105. V P Shilov, L N Astafurova, A Yu Garnov, N N Krot *Radiokhimiya* **38** 231 (1996) [c]
106. R A Penneman, L B Espri, in *Materialy 1-oi Mezhdunarodnoi Konferentsii po Mirnomu Ispol'zovaniyu Atomnoi Energii, Zheneva, 1955* (Proceedings of the First International Conference on Peaceful Use of Nuclear Energy, Geneva, 1955) (Moscow: GNTIKhL, 1959) Vol. 7, p. 435
107. K Buijs, K Louwrier *J. Inorg. Nucl. Chem.* **28** 2463 (1966)
108. N N Krot, A D Gel'man *Dokl. Akad. Nauk SSSR* **177** 124 (1967) [b]
109. N N Krot, M P Mefod'eva, T V Smirnova, A D Gel'man *Radiokhimiya* **10** 412 (1968) [c]
110. V I Blokhin, N N Krot, A D Gel'man *Radiokhimiya* **12** 792 (1970) [c]
111. D Cohen, S Fried *Inorg. Nucl. Chem. Lett.* **5** 653 (1969)
112. E A Shashukov, A A Kozlov *Radiokhimiya* **12** 237 (1970) [c]
113. M P Mefod'eva, N N Krot, T V Afonas'eva *Radiokhimiya* **19** 245 (1977) [c]
114. A V Gogolev, V P Shilov, A K Pikaev *Radiokhimiya* **31** 124 (1989) [c]
115. V P Shilov, E S Stepanova, N N Krot *Radiokhimiya* **19** 80 (1977) [c]
116. A A Chaikhorskii, M Yu Matuzenko, Yu I Belyaev *Radiokhimiya* **16** 850 (1974) [c]
117. D S Gorbenko-Germanov, I V Kozlova *Zh. Fiz. Khim.* **48** 1998 (1974) [d]
118. L Forni, D Bathemann, E J Hart *J. Phys. Chem.* **86** 255 (1982)
119. Yu A Komkov, N N Krot, A D Gel'man *Radiokhimiya* **10** 625 (1968) [c]
120. Yu A Komkov, N N Krot *Radiokhimiya* **12** 227 (1970) [c]
121. R A Penneman, J S Coleman, T K Keenan *J. Inorg. Nucl. Chem.* **17** 138 (1961)
122. V P Shilov, N N Krot, A D Gel'man *Radiokhimiya* **13** 9 (1971) [c]
123. A B Yusov, A Yu Garnov, V P Shilov, N N Krot *Radiokhimiya* **39** 515 (1997) [c]
124. Yu A Komkov, V F Peretrukhin, N N Krot, A D Gel'man *Radiokhimiya* **11** 407 (1969) [c]

125. A B Yusov, A Yu Garnov, V P Shilov, N N Krot *Radiokhimiya* **39** 519 (1997) [c]
126. A Yu Garnov, A B Yusov, V P Shilov, N N Krot *Radiokhimiya* **40** 18 (1998) [c]
127. V P Shilov, A Yu Garnov, A V Gogolev *Radiokhimiya* **40** 308 (1998) [c]
128. B B Cunningham, in *The Transuranium Elements* (Eds G T Seaborg, J J Katz) (New York; Toronto; London: McGraw-Hill, 1949) Vol. 14B, p. 1363
129. V I Spitsyn, N N Krot, M P Mefod'eva, A D Gel'man *Dokl. Akad. Nauk SSSR* **181** 128 (1968) [b]
130. V P Shilov, N N Krot, A D Gel'man *Radiokhimiya* **12** 896 (1970) [c]
131. A Yu Garnov, A B Yusov, V P Shilov, N N Krot *Radiokhimiya* **40** 213 (1998) [c]
132. N N Krot, M P Mefod'eva, T V Afonas'eva *Radiokhimiya* **19** 230 (1977) [c]
133. N N Krot, A D Gel'man, M P Mefod'eva, V P Shilov, V F Peretrukhin, V I Spitsyn *Semivalentnoe Sostoyanie Neptuniya, Plutoniya, Ameritsiya* (Heptavalent States of Neptunium, Plutonium and Americium) (Moscow: Nauka, 1977)
134. Yu M Kulyako, T I Trofimov, D A Malikov, I A Lebedev, B F Myasoedov *Radiokhimiya* **35** (5) 68 (1993) [c]
135. S G Bratsch *J. Phys. Chem. Ref. Data* **18** 1 (1989)
136. V F Peretrukhin, N N Krot, A D Gel'man *Radiokhimiya* **13** 772 (1971) [c]
137. O B Shatokhina, D P Alekseeva, V F Peretrukhin, N N Krot, N S Kirin *Radiokhimiya* **19** 824 (1977) [c]
138. P K Bhattacharyya, R Veeraghavan, R D Saini *Radiochim. Acta* **30** 217 (1982)
139. A V Gogolev, V P Shilov, A K Pikaev *Khim. Vys. Energ.* **30** 255 (1996) [e]
140. V P Shilov, A V Gogolev, A K Pikaev *Radiokhimiya* **40** 311 (1998) [c]
141. V P Shilov, N A Budantseva *Radiokhimiya* **40** 546 (1998) [c]
142. V P Shilov, A V Gogolev, A K Pikaev *Khim. Vys. Energ.* **32** 395(1998) [e]
143. V P Shilov, V B Nikolaevskii, N N Krot *Radiokhimiya* **37** (1) 32 (1995) [c]
144. W D Felix, B L Call, L M Dorfman *J. Phys. Chem.* **71** 384 (1967)
145. V P Shilov, N N Krot *Radiokhimiya* **11** 399 (1969) [c]
146. A Yu Garnov, A B Yusov, V P Shilov, N N Krot *Radiokhimiya* **39** 506 (1997) [c]
147. A V Gelis, A V Garnov, V P Shilov *Radiokhimiya* **40** 22 (1998) [c]
148. A V Gelis, A V Garnov, V P Shilov *Radiokhimiya* **40** 110 (1998) [c]
149. A B Yusov, A Yu Garnov, V P Shilov, N N Krot *Radiokhimiya* **39** 509 (1997) [c]
150. V P Shilov, A Yu Garnov, N N Krot, A B Yusov *Radiokhimiya* **39** 513 (1997) [c]
151. A A Bessonov, A V Gelis, V P Shilov, N N Krot *Radiokhimiya* **41** 516 (1999) [c]
152. Yu A Komkov, N N Krot, A D Gel'man *Radiokhimiya* **12** 692 (1970) [c]
153. A Yu Garnov, A V Gelis, A A Bessonov, V P Shilov, N N Krot *Radiokhimiya* **40** 218 (1998) [c]
154. I G Tananaev *Radiokhimiya* **31** 62 (1989) [c]
155. I G Tananaev *Radiokhimiya* **32** (5) 46 (1990) [c]
156. I G Tananaev *Radiokhimiya* **32** (2) 7 (1990) [c]
157. I G Tananaev *Radiokhimiya* **32** (5) 43 (1990) [c]
158. I G Tananaev *Radiokhimiya* **32** (5) 50 (1990) [c]
159. I G Tananaev *Radiokhimiya* **32** (1)23 (1990) [c]
160. I G Tananaev *Radiokhimiya* **34** (1) 108 (1992) [c]
161. A Yu Garnov, A V Gelis, A A Bessonov, V P Shilov *Radiokhimiya* **40** 309 (1998) [c]
162. V I Dzyubenko, V F Peretrukhin *Radiokhimiya* **19** 832 (1977) [c]
163. V I Silin, A V Kareta *J. Alloys Comp.* **271 – 273** 803 (1998)
164. V P Shilov, A B Yusov *Radiokhimiya* **35** (3) 5 (1993) [c]
165. V I Spitsyn, N N Krot *Izv. Akad. Nauk SSSR, Ser. Khim.* **4** 821 (1982) [a]
166. G V Ionova, V G Pershina, V I Spitsyn *Elektronnoe Stroenie Aktinidov* (Electronic Structure of Actinides) (Moscow: Nauka, 1986)
167. V P Domanov, G V Buklanov, Yu V Lobanov, in *Tret'ya Rossiiskaya Konferentsiya po Radiokhimii (Tez. Dokl.)* [Third Russian Conference on Radiochemistry (Abstracts of Reports)] (St Petersburg: State Unitary Enterprises Research and Production Union 'Radievyi Institut im. V G Khlopina', 2000) p. 37
168. V P Domanov, G V Buklanov, Yu V Lobanov, in *Actinides-2001 International Conference (Final Program and Abstracts), Hayama, Japan, 2001* p. 166
169. Ya V Zubavichus, Yu L Slovokhotov *Usp. Khim.* **70** 429 (2001) [*Russ. Chem. Rev.* **70** 373 (2001)]

[a] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[b] — *Dokl. Chem. (Engl. Transl.)*
[c] — *Radiochemistry (Engl. Transl.)*
[d] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[e] — *High Energy Chem. (Engl. Transl.)*