Russian Chemical Reviews **66** (9) 763 – 788 (1997) © 1997 Russian Academy of Sciences and Turpion Ltd

UDC 541.15 + 546.791 + 546.799

Radiation chemistry of aqueous solutions of actinides

A K Pikaev, V P Shilov, A V Gogolev

Contents

I.	Introduction	763
II.	General information about the mechanism of radiolysis of water	763
III.	The reactivity of actinides in aqueous solutions	764
IV.	Uranium	772
V.	Neptunium	773
VI.	Plutonium	777
VII.	Americium	782
VIII.	Other actinides	784
IX.	Conclusion	786

Abstract. The data on radiolytic transformations of ions of uranium, neptunium, plutonium, americium, curium and transcurium elements in aqueous solutions are generalised. The results of studies on the kinetics of fast reactions of these ions with primary products of water radiolysis (hydrated electron e_{aq}^-, H, OH, and O^- radicals and H_2O_2), many inorganic (Cl_2^-, NO_3, **SO_4^-, CO_3^-, O_3^-** *etc.*) **and organic free radicals are analysed. The mechanism of** γ- and α**-radiolysis of solutions of actinide ions is discussed. The bibliography includes 183 references**.

I. Introduction

Aqueous solutions of actinides are widely used in nuclear power engineering and radiochemical industry. Firstly, many systems meant for processing of nuclear materials are aqueous solutions. When these solutions are highly radioactive, actinide ions can undergo various radiolytic transformations induced by the radiation from the radionuclides present. It is clear that this can markedly influence technological processes.

Secondly, actinide ions are present in radioactive wastes (including highly radioactive liquid wastes). It is obvious that the knowledge of the regularities of radiation-induced chemical processes involving these ions is needed to correctly solve the problems of prolonged storage and disposal of these wastes: to store liquid wastes in tanks or to dispose of them in deep geological formations, to develop a technology for isolation of α-nuclides from wastes and to carry out this isolation, to dissolve plutonium-containing precipitates, *etc*.

Thirdly, in the case of accidents at nuclear power plants, radionuclides (fission-product elements, plutonium, *etc*.) can get into water; in those places where these elements are concentrated, radiolytic transformations of actinide ions can occur. These transformations may have an influence on the behaviour of actinides in the environment, and this should be taken into account in radioecological investigations.

Actinide ions can exist in aqueous solutions in a variety of oxidation states (for example, the oxidation number of americium varies from two to seven); therefore a wide range of radiation-induced redox reactions can be studied.

The radiation chemistry of aqueous solutions of actinide ions has been developed since the mid-1940s; its development started soon after the discovery of plutonium.[1] Early studies dealt with radiolysis of aqueous solutions of plutonium induced by its own α-radiation; later, radiolysis under the action of external ionising radiation (X-rays) was also investigated. Somewhat more recently, first studies dealing with the radiation chemistry of aqueous solutions of americium, uranium and neptunium ions were accomplished (see, for example Ref. 1). It should be noted that in the majority of these studies, the occurrence of a certain radiolytic transformation has been detected only qualitatively. The mechanisms of these transformations have been studied since the 1960s. Significant progress along this line has been achieved by virtue of the method of pulse radiolysis with fast recording of short-lived species (this method is described in detail in two monographs[2,3]). The results obtained up to 1980 are summarised in Ref. 1.

The present paper surveys the current state of the radiation chemistry of aqueous solutions of actinides. It is largely based on the data published during the past 15 years. The results obtained before 1980 have been surveyed in monographs[1,4] and in a handbook.[5] However, in some cases, to make the presentation more complete, some earlier studies are also discussed. This is done when their results need to receive a different interpretation due to the appearance of new information. In addition, published data on the radiolysis of solutions of actinides in nitric acid are considered in detail, because these systems are important from the practical viewpoint.

II. General information about the mechanism of radiolysis of water

Studies of aqueous solutions (including solutions of actinides) in radiation chemistry are based on the following views on the mechanism of radiolysis of water.[1,6] The primary products formed in this process are the hydrated electron e_{aq}^-, a hydrogen atom, an OH radical (its dissociated form is the O^- radical ion), molecular hydrogen H_2, hydrogen peroxide (its dissociated forms

A K Pikaev, V P Shilov, A V Gogolev Institute of Physical Chemistry of the Russian Academy of Sciences, Leninskii prosp. 31, 117915 Moscow, Russian Federation. Fax (7-095) 335 17 78.
Tel. (7-095) 330 41 70 (V P Shilov)

Received 6 September 1996
Uspekhi Khimii **66** (9) 845 – 873 (1997); translated by Z P Bobkova

are HO_2^- and O_2^{2-}) and H_{aq}^+ and OH^- ions. This can be written as follows

$$H_2O \rightsquigarrow e_{aq}^-, H, OH, H_2, H_2O_2, H^+, OH^- . \quad (1)$$

The radical species formed in the radiolysis (e_{aq}^-, H, and OH) as well as hydrogen peroxide enter into various reactions with dissolved compounds (evidently, including actinide ions) and thus cause various radiolytic transformations of the latter.†

In dilute aqueous solutions (in which concentrations of solutes are up to $\sim 10^{-3}-10^{-2}$ mol litre^{-1}), the radiation yields of the above primary products of radiolysis of water hardly depend on the concentration of the solution. The respective values for γ-radiation and for high-energy electrons are listed in Table 1.

Table 1. Radiation yields of the products [a] [molecule (100 eV)$^{-1}$] of water radiolysis induced by γ-radiation of ^{60}Co and by high-speed electrons with an energy of 1 MeV or higher.[1,6]

pH	$G_{e_{aq}^-}$	G_H	G_{OH}	G_{H_2}	$G_{H_2O_2}$	$G_{H_{aq}^+}$	G_{OH^-}
0–2	3.05	0.6	2.95	0.45	0.8	–	–
4–9	2.8–2.9	0.6	2.8–2.9	0.45	0.75	3.3–3.4	0.5–0.6
12–13	3.05	0.55	2.9	0.4	0.75	–	–

[a] Radiolysis of water also affords oxygen atoms; however, their yield is negligibly small.

In concentrated solutions, these yields do depend on the concentration, because the solute can react with the primary products in 'spurs' and tracks. In addition, the 'direct' influence of the ionising radiation on the substance becomes apparent in these solutions. It also cannot be ruled out that excited water molecules are involved in radiolytic transformations.

Actinides emit α-particles with an energy of 5–6 MeV; having passed through a material (including water), these particles form cylindrical tracks with high concentrations of primary products of radiolysis. Consequently, the yields of the latter differ markedly from those obtained in the case of γ-irradiation or irradiation with high-energy electrons. The yields of products formed upon the action of α-particles emitted by actinides have not been determined. They were measured for the α-particles with an energy of 5.3 MeV emitted by ^{210}Po (Table 2). The yields of products

Table 2. The yields of primary products of water radiolysis induced by α-particles.

Energy/ MeV	Medium [a]		$G_{e_{aq}^-} + G_H$	G_{OH}	G_{H_2}	$G_{H_2O_2}$	G_{HO_2}	Ref.
	I	II						
5.3	H_2SO_4	0.4	0.55	0.35	1.4	1.3	0.2	7
6.4		(7)	–	0.4	–	0.95	0.085	8

[a] Here and in the other Tables, the following designations are used: I — aqueous solution; II —concentration of the solution in M; the number in parentheses — pH of the medium.

obtained upon the action of α-particles with an energy of 6.4 MeV were also included in the Table. Comparison of the data presented in Tables 1 and 2 indicates that in the case of α-particles, the yields of the radical products of water radiolysis decrease, while those of the molecular products increase. Another specific feature is that HO_2 radicals (or O_2^- as the dissociated form) are formed in a relatively high yield among the primary products.

† In this review, the radiation yields of the primary products of water radiolysis are denoted by the letter G, the corresponding product being shown as the subscript (for example, $G_{e_{aq}^-}$); the overall yield of a product (with allowance for secondary reactions) is symbolised by the letter G with the product given in parentheses; the yield of the consumption of a species, for example U(IV), is denoted by $G[-\text{U(IV)}]$ and the yield of its formation is written as G[U(IV)].

When the concentration of actinides in a solution is relatively high, their α-radiation is fairly intense. This can lead to radiolytic transformations of the solutes (including actinides). Radiolysis of actinides induced by their own α-radiation is referred to as self-radiolysis.

III. The reactivity of actinides in aqueous solutions

The radiation-induced chemical processes involving actinide ions in solutions comprise their interaction with primary products of water radiolysis and with inorganic and organic free radicals resulting from the radiolysis as well as the reactions of actinide ions in unstable oxidation states (arising upon radiolytic reduction or oxidation) with stable compounds present in the solution. Rate constants for these processes have been measured by various methods;[9–13] the method of pulse radiolysis with spectrophotometric recording of short-lived species has been used most often. In some cases, conductometric recording has been employed. Some rate constants have been estimated by computer modelling of radiolytic processes.

1. The reactivity of actinide ions towards the primary products of radiolysis of water

Numerous studies have dealt with the kinetics of reactions of actinide ions with the primary products of water radiolysis. The rate constants for the reactions of uranium, neptunium, plutonium, americium, berkelium and californium ions with hydrated electrons, H, OH and O^- radicals and with hydrogen peroxide have been determined.

a. Reactions with the hydrated electron

The rate constants of the reactions of actinide ions with e_{aq}^- in acidic, nearly neutral, carbonate-containing and alkaline media are listed in Table 3. The reactions of the hydrated electron with tetra-, penta-, hexa- and heptavalent actinides (An) have large rate constants (from $\sim 2\times10^9$ to $\sim 1\times10^{11}$ litre mol^{-1} s^{-1}). The rates of the majority of these reactions are diffusion-controlled. As in the case of other diffusion-controlled reactions, there is no correlation between the rate constants and the redox potentials E° of the corresponding pairs of actinide ions, although the extreme values of E° differ by ~ 2 V, and the redox potential of the U(IV)/U(III) pair is -0.6 V.[21,34–39] A noticeable shift of the potential to the negative region observed for Th(IV) and Am(III) ions results in a decrease in the rate constants.

The reaction rates are 'insensitive' to the change in the formal charge and in the number of water molecules in the equatorial plane of the actinide ion. This can be seen in the case of complex ions of hexavalent uranium:[20] $UO_2(H_2O)_n^{2+}$, $UO_2(H_2O)_{n-1}OH^+$, UO_2(IMDA), UO_2(NTA)$^-$, $UO_2(C_2O_4)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$. The rate constants for all these ions are close to one another.

The decrease in the charge of tetravalent actinide ions in solutions containing sulfuric acid also has no significant influence on the rate constants. The formation of $AnSO_4^{2+}$ ions may not be accompanied by an increase in the electron density in the orbitals of the actinide ion accepting an electron.

Schmidt *et al.*[28] have studied the mechanism of reduction of pentavalent neptunium ions with hydrated electrons in a weakly acidic medium using pulse radiolysis with conductometric recording of short-lived species. They obtained results indicating that at pH 3.6–5.8, the reduction of NpO_2^+ to $Np(OH)^{3+}$ occurs *via* the intermediate formation of $NpO_2\cdot 6H_2O$, $Np(OH)_4\cdot 4H_2O$, $Np(OH)_3^+$ and $Np(OH)_2^{2+}$. The rate constant for the transformation of $NpO_2\cdot 6H_2O$ into $Np(OH)_4\cdot 4H_2O$ is 1.5×10^6 s^{-1}, while the rate constants for the protonation of $Np(OH)_4$, $Np(OH)_3^+$ and $Np(OH)_2^{2+}$ are 3.75×10^{10}, 4.0×10^{10}, and 4.28×10^{10} litre mol^{-1} s^{-1}, respectively. These researches also determined the pK values for the equilibria between NpO_2OH and NpO_2^+, $Np(OH)_2^{2+}$ and $Np(OH)^{3+}$. They were equal to 8.7 and 4.5, respectively.

Table 3. Rate constants for the reactions of actinide ions with the hydrated electron.

Actinide	Medium		$10^{-10}k$ /litre mol^{-1} s^{-1}	Ref.	Actinide	Medium		$10^{-10}k$ /litre mol^{-1} s^{-1}	Ref.
	I	II				I	II		
Th^{4+}	Weakly acidic solution	–	1.9	14	Np(VI)	OH^-	5.0	2.0	24, 25
						OH^-	7.5	1.1	24, 25
	$HClO_4$	0.01	< 0.01	15		OH^-	10.0	0.83	24, 25
$ThSO_4^{2+}$	Weakly acidic solution	–	1.1	14		OH^-	12.5	0.68	24, 25
					Np(V)	–	(5.3)	1.97	17
U(VI)	Acidic solution	–	7.4	16		–	(6.1)	2.13	17
						–	(3.0)	2.45	28
	–	(5.3)	1.73	17	Np(V), carbonate complex	CO_3^{2-}	0.1	0.25	27
	–	(6.8)	1.25	17		CO_3^{2-}	1.0	0.20	27
	–	(2.9)	1.7 – 7.4	18, 19		CO_3^{2-}	5.0	0.19	27
	–	(9.6)	0.45	18	Np(V)	OH^-	1.0	0.50	24, 25
	Artificial sea water	–	2.12	20		OH^-	2.0	0.61	24, 25
						OH^-	5.0	0.59	24, 25
						OH^-	7.5	0.31	24, 25
U(VI), complex with IMDA	IMDA	0.01 (10.5)	1.93	20	Np(IV)	$HClO_4$	0.023	6.3	15
	IMDA	0.05 (8.0)	3.87	20		$HClO_4$	0.038	6.3	15
	IMDA	0.25 (8.0)	3.10	20		$HClO_4$	0.055	6.0	15
U(VI), complex with NTA	NTA	0.01 (9.0)	1.67	20		$HClO_4$	0.91	6.5	15
	NTA	0.05 (9.5)	1.90	20		H_2SO_4	0.042	7.0	15
	NTA	0.25 (9.0)	2.41	20		H_2SO_4	0.06	6.1	15
U(VI), oxalate complex	$C_2O_4^{2-}$	0.01 (5.0)	2.75	20		H_2SO_4	0.68	5.8	15
					Np(IV), carbonate complex	CO_3^{2-}	0.1	0.5	27
						CO_3^{2-}	1.0	0.4	27
U(VI), carbonate complex	CO_3^{2-}	0.01 (11.4)	1.32	20		CO_3^{2-}	4.3	0.4	27
	CO_3^{2-}	0.05	1.18	21		CO_3^{2-}	6.0	0.3	29
					Pu(VII)	OH^-	1.0	3.5	24
U(IV)	$HClO_4$	0.05	6.8	22		OH^-	2.0	4.2	24
	$HClO_4$	0.1	6.5	22, 23		OH^-	5.0	2.3	24
	$HClO_4$	1.0	10.0	22		OH^-	7.5	2.0	24
	H_2SO_4	0.68	5.8	15	Pu(VI)	–	(5.6)	6.44	17
Np(VII)	OH^-	0.1	2.9	24, 25		–	(6.1)	5.76	17
	OH^-	0.5	3.2	24, 25	Pu(VI), carbonate complex	CO_3^{2-}	0.05	2.28	21
	OH^-	1.0	2.0	24, 25		CO_3^{2-}	0.1	2.3	27
	OH^-	2.0	2.1	24, 25		CO_3^{2-}	1.0	1.4	27
	OH^-	5.0	1.7	24, 25		CO_3^{2-}	5.0	0.68	27
	OH^-	7.5	1.3	24, 25	Pu(VI)	OH^-	2.0	1.9	24
	OH^-	10.0	0.88	24, 25		OH^-	5.0	2.0	24
	OH^-	12.5	0.7	24, 25		OH^-	7.5	0.66	24
Np(VI)	–	(5.3)	6.32	17	Pu(IV)	H_2SO_4	0.018 – 0.033	3.3	15
	–	(5.8)	5.43	17		H_2SO_4	0.078	12	15
	–	(2.5)	10.0	26	Pu(IV), carbonate complex	CO_3^{2-}	6.0	0.3	29
NpO_2OH^+	–	–	2.9	26					
Np(VI), carbonate complex	CO_3^{2-}	0.05	2.34	21	Am(VI)	$LiClO_4$	0.11 (5.3)	3.11	30
	CO_3^{2-}	0.1	1.9	27		$LiClO_4$	0.11 (6.0)	3.9	30
	$HCO_3^- + CO_3^{2-}$	0.5 + 0.5	1.8	27	Am(V)	$LiClO_4$	0.11 (5.2)	2.8	30
	CO_3^{2-}	1.0	1.2	27		$LiClO_4$	0.11 (6.0)	3.18	30
	CO_3^{2-}	5.0	0.62	27	Am(III)	$LiClO_4$	0.11 (5.8)	2.45×10^{-2}	30
Np(VI)	OH^-	0.5	2.3	24, 25		–	($\sim$6.0)	$\sim 3 \times 10^{-2}$	31
	OH^-	1.0	1.3	24, 25	Bk(III)	–	(5.0)	1.12×10^{-1}	32
	OH^-	2.0	1.2	24, 25	Cf(III)	–	(5.1 – 5.3)	$\geqslant 3 \times 10^{-1}$	33

Note. The following designations are used: IMDA — iminodiacetate, NTA —nitrilotriacetate.

When Np(V) is reduced to Np(IV), the structure of the neptunium ion changes (from NpO_2^+ to Np^{4+}), and this can significantly hamper the reaction. Nevertheless, the reaction rate in an acid medium is close to its diffusion limit. Therefore, it was suggested [28] that the electron transfer in this reaction is a non-adiabatic process, which yields Np(IV) in an electronically excited state as an intermediate product having an 'inappropriate' electronic configuration. Then this configuration rearranges into the configuration corresponding to a hydrolysed ion of tetravalent neptunium.

The rates of the reactions of e_{aq}^- with tetravalent uranium, neptunium and plutonium in acidic media or with heptavalent neptunium and plutonium in alkaline solutions are most probably larger than the diffusion limit. This is due to a tunnel mechanism of these reactions (detailed information about the tunnel mechanism of reactions of e_{aq}^- can be found in a monograph [40]).

In a carbonate-containing medium, the rate constants for the reactions of the hydrated electron with An(VI) depend only slightly on the concentration of carbonate ions. It has been concluded that the reaction rates are limited by the diffusion of the reacting species.[27] It was also suggested that the composition of the $AnO_2(CO_3)_3^{4-}$ complex ions does not change over the studied ranges of concentrations of carbonate ions. Therefore, variation of

the carbonate concentration influences the reaction rate only to the extent to which it changes the viscosity of the medium.

The rate constant for Np(V) is approximately an order of magnitude lower than that for Np(VI). This is due to the fact that the transition of Np(V) into Np(IV) is accompanied by a structural rearrangement.[27] The influence of the concentration of carbonate ions on the reaction rate in the case of Np(V) is also slight. It was noted that in this case, too, ion diffusion is the crucial factor.[27] The reaction of e_{aq}^- with Np(IV) occurs faster than the corresponding reaction with Np(V). This is due to the fact that Np(IV) is converted into Np(III) without a change in the structure.

The rate constants for the reactions of actinides with the hydrated electron in dilute alkaline solutions differ only slightly from those in weakly acidic solutions. The reaction rates decrease markedly at $[OH^-] \geqslant 7.5$ M. Several possible reasons for the decrease in the reaction rates in concentrated alkaline solutions have been proposed.[24] They include an increase in the viscosity of these solutions, capture of electrons in deeper traps, the formation of pairs of the $M^+ ... e_{aq}^-$ type (M^+ is an alkali metal cation) and the change in the activity coefficients of ions at high ionic strengths.

b. Reactions with a hydrogen atom

The reactions of actinide ions with hydrogen atoms are significant in acidic solutions. In these solutions, the hydrated electron reacts with H^+ being thus converted into an H atom. This reaction is fast: $k = 2.4 \times 10^{10}$ litre mol^{-1} s^{-1} for solutions with pH 2.1–6.[5] The reaction of an actinide ion with e_{aq}^- in an acidic medium is possible in the case where the product of the rate constant for the reaction of the actinide ion with the hydrated electron by the actinide concentration is comparable with the product of the rate constant for the reaction of e_{aq}^- with H^+ by the concentration of the latter. In neutral media, the reactions of H atoms are less significant because the role of the interaction of e_{aq}^- with H^+ is low and the radiation yield of H amounts to ~20% of the yield of e_{aq}^- (see Table 1). In alkaline media, processes involving H barely occur, because this species reacts with OH^- to give a hydrated electron.

The rate constants for the reactions of An(VI), An(V) and An(IV) with H are markedly lower than those for the corresponding reactions with the hydrated electron. This can be seen from the comparison of the data presented in Tables 3 and 4.

This difference can be explained by the fact that the redox potential of the H atom (−2.3 V) is less negative than that of e_{aq}^- (−2.87 V).[6] The difference between the reaction mechanisms also plays a certain role. The mechanism of the interaction of e_{aq}^- with any ion consists in electron transfer. The reactions of the H atom apparently involve the water incorporated in the hydration shell of the ion. It cannot be ruled out that this reaction starts with the insertion of H into a water molecule to give H_3O, and then electron transfer from H_3O to the central ion occurs.

Table 4. Rate constants for the reduction of actinide ions with H atoms in aqueous solutions.

Actinide	Medium		$10^{-6}\,k$ /litre mol^{-1} s^{-1}	Ref.
	I	II		
U(VI)	$HClO_4$	1.0	45	41
	H_2SO_4	0.5	7	42
U(IV)	H_2SO_4	1.0	< 1	42
Np(VI)	$HClO_4$	1.0	400	42
	–	(1.0)	< 1	26
Np(V)	$HClO_4$	1.0	< 5	41
Np(IV)	$HClO_4$	0.9	< 1	42
Pu(VI)	$HClO_4$	1.0	200	42
Pu(IV)	$HClO_4$	3.0	17	42
	H_2SO_4	0.6	45	42
	H_2SO_4	1.6	61	42
Am(VI)	Solution of perchloric acid	–	1600	43
Am(V)	$HClO_4$	1.0	200	43

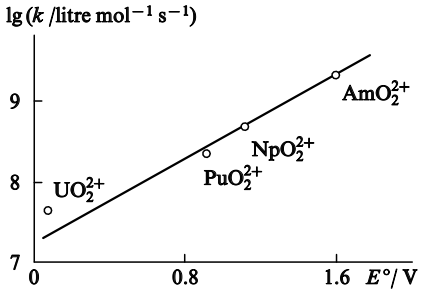


Figure 1. Dependence of the rate constants for the reactions of H atoms with actinyl ions in a 1 M solution of $HClO_4$ on the redox potentials of the AnO_2^{2+}/AnO_2^+ pairs.

The dependences of the logarithms of the rate constants for the reactions of H with all the AnO_2^{2+} ions studied on the redox potentials of the AnO_2^{2+}/AnO_2^+ pairs (or on the free energy of the reaction) are nearly linear (Fig. 1). Thus, the mechanisms of these reactions are identical and their rates are not controlled by diffusion. However, since there are no data on the rate of the exchange of water molecules coordinated by actinyl ions, this mechanism cannot be interpreted in detail.

For the reactions of actinyl ions with H, no linear correlation between the logarithm of the rate constant and the E° value is observed. It should also be noted that the rate constants for the reactions of H with NpO_2^+ and AmO_2^+ differ by two orders of magnitude, although the difference between the E° values for the Np(V)/Np(IV) and Am(V)/Am(IV) pairs is not that large.

The reactions considered above are reduction processes. Oxidation by H atoms is also known; for example, it reacts with U(V), Np(III) and Pu(III). The rate constants for these reactions are presented in Table 5. It can be seen that on passing from a solution in perchloric acid to a solution in sulfuric acid the rate constants for Pu(III) and Np(III) increase. This is due to the fact that the redox potential of the An(IV)/An(III) pair in sulfuric acid is smaller than that in perchloric acid and the potential of the Np(IV)/Np(III) pair is also smaller. In the case of U(V), the nature of the acid has apparently no influence on the rate of the process.

Table 5. Rate constants for the oxidation of actinide ions with H atoms in aqueous solutions.[42, 44]

Actinide	Medium		$10^{-6}\,k$ /litre mol^{-1} s^{-1}
	I	II	
U(V)	$HClO_4$	0.1	~400
	H_2SO_4	0.4	10–400
Np(III)	$HClO_4$	1.0	63
	H_2SO_4	1.0	190
Pu(III)	$HClO_4$	3.0	< 1
	$HClO_4 + H_2SO_4$	0.2 + 1.8	6

Evidently, oxidation with an H atom is not an elementary process. It may involve the intermediate formation of a hydride ion as has been observed for the oxidation of Fe^{2+} ions (see, for example, Ref. 6).

c. Reactions with OH and O^- radicals

The OH radical exists in acidic, neutral and weakly alkaline media.

In an alkaline medium, electrolytic dissociation affords the O^- radical ion. The pK value for the corresponding equilibrium is 11.9 (see, for example, Ref. 6). The rate constant for the $OH + OH^-$ reaction is large,[5] 1.2×10^{10} litre mol^{-1} s^{-1}; therefore, at pH > 13, it is the O^- radical ion that reacts with dissolved

Table 6. Rate constants for the reactions of actinide ions with OH radicals in aqueous solutions.

Actinide	Medium		$10^{-8}k$ /litre mol^{-1} s^{-1}	Ref.
	I	II		
U(III)	Acidic	–	4.1	45
U(IV)	$HClO_4$	0.1	9.2	22, 46
	$HClO_4$	1.0	8.6	22, 46
Np(III)	$HClO_4$	1.0	40	47
Np(IV)	$HClO_4$	1.0	3.2	48
Np(V)	$HClO_4$	(2.52–2.95)	5.7	48
	$HClO_4$	0.1	4.4	48
	$HClO_4$	1.0	4.3	48
	–	(< 4.0)	0.43	26
	–	(4.75)	2.7	49
	–	(4.23)	5.9	49
	–	(3.64)	4.2	49
	$HClO_4$	0.1	5.8	49
Pu(III)	$HClO_4$	1.0	4.2	50
	–	(4.0)	18.3	51
Pu(IV)	$HClO_4$	3.0	2.4	47
Am(III)	–	(4.0)	3.2	52
	–	(2.0)	3.4	52
	–	(1.0)	11.0	52
	$HClO_4$	1.0	16.0	52
	$LiClO_4$	0.11, (5.1)	4.1	29

substances including actinides in dilute solutions (with concentrations of no more than $\sim 10^{-3}$ mol litre^{-1}).

The results of studies on the kinetics of the reactions of OH with An(III), An(IV) and An(V) and the reactions of O^- with An(V) and An(VI) are presented in Tables 6 and 7. The rate constants of these reactions do not depend on the redox potentials of the An^{n+1}/An^n pairs; for example, the potentials of the U(IV)/U(III) and Am(IV)/Am(III) pairs are -0.52 and 2.62 V, respectively, whereas the rate constants for the reactions of U(III) and Am(III) are 4.1×10^8 and 3.4×10^8 litre mol^{-1} s^{-1} (Table 6). Structural rearrangements also have no influence on the reaction rate [oxidation of Np(IV) and Np(V) provide an example]. It is noteworthy that on passing from a weakly to a strongly acidic medium the rate constant of the reaction of OH with Pu(III) decreases about four-fold, whereas the rate of a similar reaction with Am(III) increases by the same factor.

Table 7. Rate constants for the reactions of penta- and hexa-valent neptunium ions with O^- radical ions in aqueous solutions of LiOH. [53, 54]

Ion	[LiOH] [a]	$10^{-7}k$ [b]	Ion	[LiOH] [a]	$10^{-7}k$ [b]
Np(V)	1.0	47	Np(VI)	1.03	4.2
Np(VI)	0.033	8.0		1.72	4.2
	0.072	5.4		2.0	5.1
	0.24	3.6		0.5–1.7	6.1
	0.51	4.2		(in NaOH)	

[a] Concentration is expressed in mol litre^{-1}, [b] k — in litre mol^{-1} s^{-1}.

Two possible mechanisms for the oxidation with OH radicals have been proposed. According to one of them, the reaction rate is limited by abstraction by the OH radical of an H atom from a water molecule in the hydration shell of the ion, as has been postulated by Berdnikov [55] for transition metal ions in general. According to the other mechanism, the radical adds to an actinide ion, and after that, a rearrangement in its inner shell occurs, which is accompanied by the elimination of OH^-. The latter mechanism was proposed by Golub *et al.* [45] and supported by Lierse *et al.*[51]

d. Reactions with hydrogen peroxide

Hydrogen peroxide can act, with respect to actinide ions, both as an oxidising and a reducing agent. This depends on the pH of the solution and on the redox potential of the actinide pair in this solution. Recall that depending on the pH, hydrogen peroxide exists as H_2O_2, HO_2^- (the pK value for the corresponding equilibrium is 11.9 [6]) or O_2^{2-} (this ion is formed at pH > 13.5). The rate constants for the oxidation of actinide ions with hydrogen peroxide in aqueous solutions are presented in Table 8.

Table 8. Rate constants for oxidation of actinide ions with hydrogen peroxide in aqueous solutions.

Actinide	Medium		k /litre mol^{-1} s^{-1}	Ref.
	I	II		
U(III)	$HClO_4$	0.5	2×10^5	45
U(IV)	$HClO_4$	1.0	3.88	56
	H_2SO_4	0.98	1.62	56
	H_2SO_4	0.4	0.41	57
	HCl + NaCl	0.05 + 1.95	23.3	58
	HCl + NaCl	0.1 + 1.9	8.0	58
	HCl + NaCl	0.25 + 1.75	2.4	58
	HCl + NaCl	0.316 + 1.684	1.9	58
	HCl + NaCl	0.5 + 1.5	1.1	58
	HCl + NaCl	1.0 + 1.0	0.45	58
	HCl + NaCl	1.5 + 0.5	0.3	58
	HCl + NaCl	0.5 + 1.5	0.24	58
U(V)	Acidic solution	–	55	59
Np(III)	Solution of perchloric acid		30–38	56
Np(IV)	Solution of nitric acid		0.08	60
Np(V)	HNO_3	7.5	0.45 [a]	61
Pu(III)	Solution of sulfuric acid		0.055	62

[a] Estimated from a figure presented in Ref. 61.

Comparison of the rate constants with the redox potentials of the corresponding pairs of actinide ions shows a clear-cut tendency for the constants to decrease upon an increase in the potentials. This, in principle, may attest to an outer-sphere mechanism of these processes. However, the oxidation of Np(III) results in the accumulation of Np(V), *i.e.* a two-electron process occurs, and only after some period, Np(IV) appears in the solution as a result of the reaction between Np(III) and Np(V).

Table 8 presents the rate constant for the bimolecular oxidation of Pu(III); however, in a large number of experiments,[62] the reaction rates were described by the equation:

$$-\frac{d[Pu(III)]}{dt} = k[Pu(III)]^2[H_2O_2] \,. \qquad (2)$$

The researchers cited [62] believe that the mechanism of this reaction includes the formation of a peroxide complex, which slowly decomposes to give Pu(IV).

Oxidation of An(IV) is a single-electron process yielding An(V) and OH. This is confirmed by the fact that the oxidation of U(IV) by hydrogen peroxide in a solution saturated with benzene gives rise to phenol.[57] Oxidation of An(V) in acidic solutions affords only An(VI) and OH. However, it should be noted that during γ-radiolysis in an alkaline solution, Np(V) reacts with hydrogen peroxide to give a peroxo-complex.[63]

The reduction of actinide ions with hydrogen peroxide results in the formation of HO_2 in addition to the reduced ions. Apparently, the reduction involves intermediate formation of a peroxo-complex.

The rate constants for the reduction of actinide ions with hydrogen peroxide in aqueous solutions are listed in Table 9. Their magnitudes increase with an increase in the difference between the redox potentials of the actinide pair and O_2/H_2O_2. This regularity is especially typical of Pu(IV). The difference between the formal potentials of the Pu(VI)/Pu(V) and O_2/H_2O_2 pairs in an acidic medium is 0.24 V, while that for the same reagent in a solution of $NaHCO_3$ is 0.15–0.20 V; the corresponding rate constants differ by 4 orders of magnitude. The formation of peroxo-complexes mentioned above also has some influence on the reaction rate.

Table 9. Rate constants for reduction of actinide ions with hydrogen peroxide in aqueous solutions.

Actinide	Medium		k /litre mol^{-1} s^{-1}	Ref.
	I	II		
U(VI)	–	(5.2)	1.39×10^4 (see [a])	17
Np(VII)	–	(8.7)	4.0×10^4	64
	–	(10.0)	6.2×10^4	64
	–	(12.4)	2.4×10^3	64
	LiOH	0.1, (12.86)	5.8×10^2	64
	LiOH	1.0, (13.7)	3.7×10^2	64
Np(VI)	–	(9.2)	5.0×10^4	64
	–	(10.0)	2.1×10^4	64
	–	(11.0)	4.0×10^3	64
	LiOH	0.1, (12.86)	9.5×10^2	64
	LiOH	1.0, (13.7)	1.4×10^2	64
	Solution of perchloric acid		4.45	56
	Weakly acidic solution		5.9×10^5	17
	HNO_3	7.5	2.2×10^{-1} (see [b])	61
Np(V)	HNO_3	4.5	2.5×10^{-2}	65
	HNO_3	6.0	3.5×10^{-2}	61
	HNO_3	7.5	7.7×10^{-2}	61
	HNO_3	8.4	8.9×10^{-2}	61
Pu(VI)	$HClO_4$	1.0	3.2×10^{-3}	56
	HNO_3	1.0	6.2×10^{-3}	56
	H_2SO_4	0.18	3.1×10^{-3}	56
	$NaHCO_3$	0.05	7.0×10^3 (see [a])	66
	$NaHC_3$	0.05	~ 50	66
Pu(IV)	$HClO_4 + Na_2SO_4$	0.3 + 0.4	16.0 (see [c])	67
	$HClO_4$	1.0	8.64×10^5 (see [d])	68
Pu(IV),[f]	$HClO_4$	1.5	2.25×10^{-4} (see [e])	69
Pu(IV)	HNO_3	0.98 – 1.96	1.0×10^{-1}	70
Am(VI)	$HClO_4$	0.98	1.92×10^4	71
Am(V)	$HClO_4$	0.1	4.1×10^{-3}	56
	$HClO_4$	0.2	9.0×10^{-3}	56
Am(IV)	–	(4.0)	1.4×10^6	52

[a] Rate constant for the formation of the peroxo-complex. [b] Estimated from a figure presented in Ref. 61. [c] Rate constant in the equation $-d[Pu(III)]/dt = k[Pu(IV)]^2[H_2O_2]$. [d] Rate constant for the formation of the peroxo-complex of Pu(IV) from the equation $d[complex]/dt = k[Pu(IV)]^2[H_2O_2]$. [e] First-order rate constant, s^{-1}. [f] Peroxide complex (decomposition).

In alkaline solutions in which the peroxide exists as HO_2^- and actinide anions are present, not only is the difference between the redox potentials significant but is the charge of the anion also. As the pH value increases, the rate constants, for example, for Np(VII) and Np(VI), decrease; this is due to the decrease in the difference between the potentials (the redox potentials of actinide pairs change more sharply than that of the O_2/H_2O_2 pair). However, the rate constants for Np(VII) and Np(VI) at identical pH values are close, although the potentials of the Np(VII)/Np(VI) and Np(VI)/Np(V) pairs differ by ~ 0.4 V. This behaviour may be due to the fact that the charge of the Np(VII)-containing anion is 3–, while that of the Np(VI) anion is 2–.

2. Reactivity of actinide ions towards 'secondary' inorganic and organic free radicals

In aqueous solutions, the primary radical products resulting from water radiolysis (e_{aq}^-, H, OH, O^-) react with dissolved compounds and are thus converted into 'secondary' radicals. For example, the reaction of e_{aq}^- with NO_3^- affords NO_3^{2-} radical ion, while reactions of OH with HSO_4^- or $HCOO^-$ give rise to SO_4^- or CO_2^-, respectively. In relatively concentrated solutions (more than ~ 0.1 mol litre^{-1}), 'secondary' radicals can also arise *via* the direct action of the ionising radiation on the dissolved substance. The formation of the NO_3 radical upon direct ionisation of the nitrate ion can serve as an example.

The secondary radicals possess various redox properties. Data on the redox potentials of these radicals have been reported in a number of studies.[72–74] The potentials of the secondary radicals SO_4^-, NO_3 and Cl_2^- are comparable with those of the OH radical (the E° values of the latter are 1.9, 2.32 and 2.73 V in a 1 M solution of OH^-, at pH 7 and in a 1 M solution of H^+, respectively[6]). Therefore, the transformation of the OH radical into any other radical decreases the probability of accumulation of actinide ions in higher oxidation states during radiolysis. Note also that the introduction of certain substances in the solution makes it possible to convert the OH radical into a 'secondary' radical acting as a reducing agent. For example, the reaction of OH with formate ion affords the CO_2^- radical ion, which possesses strong reducing properties. The hydrated electron can be converted into an oxidising radical; for example, by the reaction with the peroxodisulfate ion (this reaction yields SO_4^-). A significant radiation-induced chemical process is the reaction of e_{aq}^- with dinitrogen oxide; in this reaction, the OH radical (or O^-) appears in the solution instead of the hydrated electron.

The SO_4^-, NO_3, CO_3^-, Cl_2^-, HO_2, COOH and some other radicals also belong to the group of 'secondary' radicals.

a. Reactions with sulfate radicals

The SO_4^- radical ions are formed during radiolysis of solutions of sulfuric acid or sulfates upon the oxidation of HSO_4^- ions with OH radicals and upon the direct action of the ionising radiation on the sulfate ions. These radical ions can also result from irradiation of solutions containing peroxodisulfate ions.

The acid form of SO_4^- is the HSO_4 radical. The pK value for its dissociation is unknown. One may only believe that in neutral and probably in weakly acidic solutions, the sulfate radical exists mostly as SO_4^-.

The rate constants for the reactions of actinide ions with sulfate radicals are listed in Table 10. It can be seen that these radicals rapidly oxidise tri- and penta-valent actinide ions and are much less reactive towards tetravalent actinide ions. The rates of reactions with U(V) and Np(III) are most likely diffusion-controlled. In the sequence Np(III) – Pu(III) – Am(III), the reactivity decreases, owing to an increase in the redox potential of the An(IV)/An(III) pair.

The main difference between the reactivities of the SO_4^- and OH radicals is manifested in their reactions with tetravalent actinide ions. Obviously, the oxidation of non-oxygenated ions into dioxo-ions cannot be regarded as an elementary chemical reaction. It may consist of two steps, which can formally be represented as the formation of an An^{5+} ion and its subsequent hydrolysis. Even in the case of U(IV), which is relatively easy to oxidise, no linear correlation exists between the measured rate constant for the pseudo-first-order reaction and the concentration of the metal ions. It cannot be ruled out that the reaction with the

Table 10. Rate constants for the reactions of actinide ions with sulfate radicals.

Actinide	Medium		$10^{-6}\,k$ /litre mol^{-1} s^{-1}	Ref.
	I	II		
U(V)	H_2SO_4	1.5	7.7×10^3	75
U(IV)	H_2SO_4	2 – 5	$(1-8) \times 10$ (see [a])	11
Np(V)	H_2SO_4	2.0	7.0×10^2	49
Np(IV)	Solution of sulfuric acid		< 5.0	10
Np(III)	H_2SO_4	3.0	3.5×10^3	76
Pu(IV)	Solution of sulfuric acid		< 5.0	10
Pu(III)	H_2SO_4	5.0	5.0×10^2	77
Am(V)	$MgSO_4 + HClO_4$	1.8 + 0.2	7.0×10^2	76
Am(III)	$H_2SO_4 + Na_2S_2O_8$	1.0 + 1.0	2.5×10	See [b]

[a] The k value depends on the concentration of U(IV); it decreases as this concentration increases. [b] Unpublished results of the authors of this review.

OH radical involves the intermediate formation of $An(OH)^{4+}$, which apparently facilitates oxygenation. Perhaps this pathway is not characteristic of the sulfate radical.

b. Reactions with the NO_3 radicals

The NO_3 radicals arise in the radiolysis of acidic or neutral solutions containing nitrate ions due to the oxidation of nitric acid molecules and (to a markedly lesser extent) nitrate ions by OH radicals, or due to the direct action of ionising radiation on NO_3^- and HNO_3 (see, for example, Ref. 78).

The rate constants for the reactions of actinide ions with NO_3 radicals in aqueous solutions are presented in Table 11. The published data are limited to Np(V), Pu(III) and Am(V); however, some conclusions and predictions can also be made about the reactivity of the NO_3 radical with respect to other actinides.

Table 11. Rate constants for the reactions of actinide ions with NO_3 radicals.

Ion	Medium		$10^{-8}\,k$ /litre $mol^{-1}\,s^{-1}$	Ref.
	I	II		
Np(V)	HNO_3	1.0	8.8	49
	HNO_3	2.0	7.0	49
	HNO_3	5.0	8.4	49
	$HNO_3 + LiNO_3$	1.0 + 3.0	9.2	49
	$HNO_3 + LiNO_3$	1.0 + 6.0	6.4	49
Pu(III)	HNO_3	2.0	2.5	77
Am(V)	HNO_3	2.5	2.5	76

In the case of reactions of neptunoyl ions, the concentration of nitric acid or nitrate ions exerts no significant influence on the rate constant. A similar behaviour can be proposed for reactions of other actinoyl ions with this radical. The Pu(III) ions are oxidised relatively rapidly by the NO_3 radical. The Np(III) ions having a smaller redox potential should react with a larger rate constant. The potentials of the Am(IV)/Am(III) and NO_3/NO_3^- pairs are commensurable; therefore, it may be expected that Am(III) would react with NO_3 at a low rate. The reactions of An(IV) with NO_3 occur apparently at lower rates than An(IV) + SO_4^-. The rate of the reaction between U(V) and NO_3 should be diffusion-controlled. This is attested by the fact that non-charged $HSeO_3$ radicals having a smaller redox potential react with U(V) at a diffusion-controlled rate: the rate constants for the U(V) + $HSeO_3$ reaction in 0.1 and 0.9 M solutions of $HClO_4$ are 1.4×10^{10} and 1.8×10^{10} litre $mol^{-1}\,s^{-1}$, respectively.[75]

c. Reactions with molecular ions of halogens and with $(CNS)_2^-$

The Cl_2^-, Br_2^- and I_2^- molecular ions derived from halogens and $(CNS)_2^-$ derived from the pseudo-halogen arise during the radiolysis of aqueous solutions as a result of oxidation of halide and thiocyanate ions with OH radicals. These species are formed in several steps: first, OH adds to Hal^- (Hal^- is a halide or thiocyanate ion); the resulting $HalOH^-$ radical ion decomposes to give Hal and OH^-, and then Hal reacts with Hal^-. In addition, these radical ions can result from oxidation of Hal^- with SO_4^- and NO_3, from reduction of Hal_2 (for example, with e_{aq}^-) and from the direct action of ionising radiation on Hal^-.

The rate constants for the reactions of the radical ions Hal_2^- with actinide ions are listed in Table 12. The following general conclusions about the reactivity of these radical ions can be drawn.

As a rule, these radical ions are less reactive with respect to actinide ions than sulfate and nitrate radicals. This is due to the fact that the redox potentials of Hal_2^- are smaller.

Almost all the reactions involving Hal_2^- are characterised by rate constants smaller than those of the diffusion limit; in this case, it may be expected that the free energies of the reactions (or the difference ΔE° between the redox potentials of the reacting species) would have a substantial influence. The logarithms of

Table 12. Rate constants for the reactions of actinide ions with Cl_2^-, Br_2^-, I_2^- and $(CNS)_2^-$ radical ions.

Actinide	Radical ion	Medium		$10^{-5}\,k$ (see [a])	Ref.
		I	II		
U(V)	Cl_2^-	$HCl + HClO_4 + UO_2(ClO_4)_2$	0.1 + 0.7 + + 0.1	4×10^4	76
	Cl_2^-	NaCl	1.0, (3)	6.5×10^3	79
	$(CNS)_2^-$		(1.0)	1.46×10^4	80
U(III)	Cl_2^-	$HClO_4 + HCl$	0.5 + 0.1	4.8×10^4	45
	Br_2^-	$HClO_4 + NaBr$	0.5 + 0.1	3.4×10^4	45
	I_2^-	$HClO_4 + KI$	0.9 + 0.1	1.2×10^4	81, 82
	I_2^-	$HClO_4 + KI$	0.9 + 0.1	1.25×10^4	45
	$(CNS)_2^-$	$HClO_4 + NaCNS$	0.5 + 0.1	1.4×10^4	45
Np(V)	Cl_2^-	HCl	1.0	3.1×10	49
	Cl_2^-	HCl	3.0	1.1×10^2	49
	Cl_2^-	$HCl + LiCl$	0.5 + 5.0	3.0×10^2	49
	Cl_2^-	$HCl + LiClO_4$	0.9 + 4.0	3.0×10^2	49
	Cl_2^-	$HCl + MgCl_2$	0.7 + 1.5	3.0×10^2	49
	Cl_2^-	$HCl + LiCl$	0.8 + 3.0	1.4×10^2	49
	Cl_2^-	NaCl	1.0, (3.0)	2.38×10^3	79
	Br_2^-	HBr	1.0	< 10	49
Np(III)	Cl_2^-	$HCl + HClO_4$	0.1 + 0.9	1.6×10^4	82
	Br_2^-	HBr	1.0	1.1×10^3	82
	I_2^-	$NaI + HClO_4$	0.1 + 0.9	5.0×10	82
Pu(III)	Cl_2^-	HCl	1.0	3.0×10^2	77
	Cl_2^-	HCl	3.0	6.0×10^2	77
	Cl_2^-	HCl	5.0	1.2×10^3	77
	Cl_2^-	$HCl + HClO_4$	0.01 + 5.0	4.0×10^2	77
	Cl_2^-	$HCl + H_2SO_4$	0.01 + 2.5	2.3×10^2	77
	Cl_2^-	NaCl	1.0, (3.0)	4.8×10^2	79
	Br_2^-	HBr	1.0	1.6×10	77
Am(III)	Cl_2^-	NaCl	1.0, (3.0)	1.5	79
	Cl_2^-	NaCl	1.0, (3.0)	3.2	79

[a] The constants are expressed in litre $mol^{-1}\,s^{-1}$.

the rate constants for similar reactions of Np(III) and Pu(III) with Cl_2^-, Br_2^- and I_2^- radical ions depend linearly on ΔE° (Fig. 2).

The rates of reactions of Hal_2^- with tri- and pentavalent actinide ions are greater than those for tetravalent actinide ions [for example, according to our data, the presence of $\sim 10^{-2}$ mol · litre^{-1} of Np(IV) or Pu(IV) has no influence on the rate of consumption of Cl_2^-], because oxidation of the latter is hampered due to the difference between the structures of the initial and oxidised ions. The mechanisms of the reactions of Hal_2^- with actinide ions include a step of formation of short-lived non-oxygenated and monooxygenated ions; the probability of transformation of these ions into final products (actinoyl ions) depends on their stability.

Oxygenated ions are also formed upon oxidation of some other ions, for example, Ti(III) and V(III). The rate constants for the reactions of Cl_2^- with the Ti(III)-, Np(III)- and Pu(III)-contain-

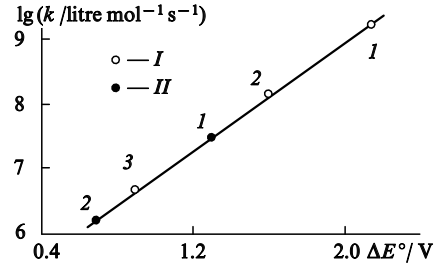


Figure 2. Dependence of the rate constants for the reactions of trivalent neptunium (*I*) and plutonium (*II*) with Cl_2^- (*1*), Br_2^- (*2*) and I_2^- (*3*) on the difference between the redox potentials of the reacting species.

ing aqua-ions are 1.1×10^7, 1.0×10^9 and 3.0×10^7 litre mol^{-1} s^{-1}, respectively, although the redox potentials for the Ti(IV)/Ti(III), Np(IV)/Np(III) and Pu(IV)/Pu(III) pairs are equal to 0.1, 0.14, and 0.97 V, respectively. The redox potential of the V(IV)/V(III) pair is 0.34 V, and the reaction of Cl_2^- with the V(III) aqua-ion is slower ($k < 10^6$ litre mol^{-1} s^{-1}) than the Ti(III) + Cl_2^- reaction. Evidently, the oxidation of Np(III) and Pu(III) ions is not accompanied by a structural rearrangement and, therefore, it is more efficient than the oxidation of the 3*d*-element ions under consideration (even though in the case of actinide ions, valence electrons are transferred from the lower *f* orbitals).

In concentrated solutions of chlorides, inner-sphere chloro-complexes are formed; they are more reactive towards Cl_2^- than the corresponding aqua-ions. The logarithms of the rate constants are proportional to the concentration of chloride ions. These correlations have been obtained for the reactions of Cl_2^- with Np(V), Pu(III), Ce(III) and with some ions of 3*d* elements.

d. Reactions with the CO_3^- radical ion

The CO_3^- radical ions are formed during radiolysis of carbonate- and hydrogencarbonate-containing solutions. They result from reactions of the OH or O^- radicals with carbonate or hydrogencarbonate ions or from the direct action of ionising radiation on these ions. If the solution contains peroxodisulfate ions, CO_3^- can also arise *via* the reaction of SO_4^- with the carbonate ion. Recall that carbonates are always present as an impurity in solutions of alkali; radiolysis of these solutions can also afford CO_3^-. The rate constants for the reactions of actinide ions with the CO_3^- radical ion in aqueous solutions are presented in Table 13. It should be emphasised that, depending on the concentrations of the solutes, CO_3^- reacts in carbonate, hydrogencarbonate and alkaline carbonate solutions with carbonate, hydroxocarbonate and hydroxo-complexes of actinides and with their oxo-anions. In these reactions, the radical ion under consideration acts as an oxidising agent.

The similarity of the electrostatic properties and structures of ions of 5*f* elements (including these ions in carbonate complexes) accounts for the linear correlations between the logarithms of rate constants and the ΔE° values of the reacting species. These correlations hold for the reactions of CO_3^- with the carbonate complexes of Am(III), Ce(III), Pu(III)[29] and U(V), Np(V), Pu(V).[21]

Table 13. Rate constants for the reactions of actinide ions with CO_3^- radical ions.

Actinide	Medium		$10^{-5}\,k$ /litre mol^{-1}s^{-1}	Ref.
	I	II		
U(V)	K_2CO_3	0.05	4.9×10^4	21
U(IV)	Saturated solution of $KHCO_3$	–	1.4×10^2	29
Np(VI)	Na_2CO_3 + NaOH	0.5 + 1.0	9.0	53
Np(V)	Na_2CO_3 + NaOH	0.5 + 0.2	1.8×10^2	53
	Na_2CO_3 + NaOH	0.5 + 0.6	2.4×10^2	53
	Na_2CO_3 + NaOH	0.5 + 1.0	4.4×10^2	53
	Na_2CO_3	0.05	1.5×10^2	21
Np(IV)	Carbonate solution		$< 5 \times 10$	10
Np(III)	K_2CO_3	1.0	3.3×10^4	29
	K_2CO_3	3.0	1.4×10^4	29
Pu(VI)	Na_2CO_3	0.01	1.5×10^2	83
	Na_2CO_3	5×10^{-3}	5.0×10	83
Pu(V)	Na_2CO_3	0.05	2.7×10^2	21
Pu(IV)	Carbonate solution		$< 5 \times 10$	10
Pu(III)	K_2CO_3	1.0	7.0×10^3	29
	K_2CO_3	1.1	5.6×10^3	29
	K_2CO_3	4.3	6.7×10^3	29
Am(III)	K_2CO_3	3.0	2.5×10^2	29
	K_2CO_3	4.6	2.7×10^2	29
	K_2CO_3	6.0	1.5×10^2	29

The influence of the concentrations of the carbonate ions and of alkali on the reaction rate is associated with changes in the compositions of the coordination spheres of the ions and, as a consequence, in their electrostatic charges and redox potentials.

e. Reactions with the HO_2, O_2^- and O_3^- radicals

The HO_2 and O_2^- radicals can arise in aqueous solutions containing oxygen (mostly in reactions of oxygen with H and e_{aq}^-). The yields of the HO_2 radicals as a primary product of radiolysis induced by heavy charged particles (including the α-particles emitted by actinides) are relatively high (see Table 2). The HO_2 and O_2^- radicals are in equilibrium with each other (pK is 4.7[6]). The O_3^- ion radicals are formed in an alkaline medium upon the reaction of O^- with oxygen. Besides, HO_2 and O_2^- are intermediate species formed in the reduction reactions involving hydrogen peroxide, and O_3^- or its acid form HO_3 [the pK value for the corresponding equilibrium is 6.15 (see Ref. 6)] also arise when ozone reacts with e_{aq}^- and H.

The rate constants for the reactions of actinide ions with HO_2, O_2^- and O_3^- radicals are listed in Table 14. Two types of reactions with actinide ions are known for HO_2 and O_2^-, namely, electron transfer and formation of a complex. It is also noteworthy that the lifetime of O_2^- increases with increase in the pH, and for concentrations of alkali of more than 1 M, it reaches tens of seconds and

Table 14. Rate constants for the reactions of actinide ions with HO_2, O_2^- and O_3^- radicals.

Actinide	Medium		$10^{-3}\,k$ /litre mol^{-1} s^{-1}	Ref.
	I	II		
Reactions with HO_2				
Th(IV)[a]	–	(1.0)	1.8×10^3	84
Th(IV) – HO_2	–	(1.0)	8.0×10^2	84
U(VI)[b]	–	(1.0)	1.5×10^2	85
U(VI) – HO_2	–	(1.0)	9.0×10^2	85
Np(V)	Acidic solution		1.1	1
Am(IV)	–	(1.0)	6.4×10^4	52, 87
	–	(2.0)	5.2×10^4	52, 87
	–	(3.2)	3.2×10^4	52, 87
	–	(4.4)	2.7×10^4	52, 87
Reactions with O_2^-				
Np(VII)	–	(8.80)	1.4×10^2	64
	–	(8.97)	9.5×10	65
	–	(9.50)	6.5×10	64
	–	(9.76)	7.6×10	64
	–	(10.0)	5.2×10	64
	–	(10.7)	3.4×10	64
	–	(11.0)	2.6×10	64
	LiOH	0.1	7.2	64
	LiOH	0.2	4.7	64
	LiOH	0.5	8.8×10^{-1}	64
	LiOH	1.0	1.3	64
Np(VI)	–	(9.18)	1.4×10^2	64
	–	(10.46)	6.5×10	64
	–	(10.93)	5.3×10	64
	–	(11.94)	1.45×10	64
	LiOH	0.1	1.5	64
	LiOH	0.2	6.0×10^{-2}	64
	LiOH	0.5	2.0×10^{-2}	64
	LiOH	1.0	8.0×10^{-3}	64
Reactions with O_3^-				
Np(VI)	LiOH	0.2 – 2.0	2.1×10^2	86
Np(V)	LiOH	0.2 – 2.0	2.0×10^3	86

[a] The reactions yields a complex of Th(IV) with HO_2. [b] The reaction yields a complex of U(VI) with HO_2.

longer. Therefore, even relatively slow reactions of O_2^- with actinide ions can occur in alkaline solutions.

Attention is drawn to the fact that the reduction of Np(VI) with O_2^- radical ions occurs faster than reduction of Np(VII) under comparable conditions, although the redox potentials of the Np(VII)/Np(VI) and Np(VI)/Np(V) pairs are 0.6 and 0.15 V, respectively. In all probability, this is due to the different charges of the Np(VII)- and Np(VI)-containing ions (3− and 2−, respectively) and different structures of these ions in solution.

Reduction reactions of actinide ions with O_3^- radicals are unknown. However, decomposition of these radicals in aqueous solutions may yield hydrogen peroxide, which possesses reducing properties.

f. Reactions with organic free radicals

Organic free radicals are generated during radiolysis of aqueous solutions containing organic compounds. In concentrated solutions, they can arise from the direct action of ionising radiation on a dissolved compound.

Information on the reactivity of organic free radicals towards actinide ions is especially important for predicting the behaviour of extraction systems used in the radiochemical industry. All the organic free radicals studied exhibit reducing properties in reactions with actinide ions. The rate constants for these reactions are listed in Table 15.

It can be seen that the rates of reactions of COOH, $(CH_3)_2COH$ and electron adducts of *o*-phenanthrolinium, 2,2′-bipyridinium and 4,4′-dipropyl-2,2′-bipyridinium with actinide ions are high. It has been assumed that these reaction rates are limited by diffusion. Calculation of the diffusion limit rate constant for the Np(VI) + $(CH_3)_2COH$ reaction based on the Smolukhovskii equation has shown [91] that the calculated and experimental values are close to each other. In addition, it was found that the activation energies for the reactions of U(VI) with the electron adducts of *o*-phenanthrolinium and 2,2′-bipyridinium are 10 and 16.7 kJ mol^{-1}, respectively. These magnitudes are typical of reactions the rates of which are diffusion-controlled or are close to the diffusion limit.

Uranium, neptunium, plutonium and americium ions react with the H adducts of *o*-phenanthrolinium and 2,2′-bipyridinium much more slowly than with the corresponding electron adducts. This is due most likely to the difference between the structures of the electron and H adducts. Thus it has been suggested [92] that the electron adduct of *o*-phenanthroline is protonated at the second nitrogen atom in the molecule, whereas in the case of the H adduct, the additional hydrogen atom adds to one of the ring carbon atoms. Therefore, the excess electron in the electron adducts is delocalised over the aromatic π-system, whereas in H adducts, this system is broken to give a cyclodienyl type radical. In the former case, the transfer of an electron occurs readily, while in the latter case it is hampered.

It should be emphasised that the reactivity of actinide ions towards organic free radicals has been markedly less studied than their reactivity with respect to inorganic radicals. This is especially true for the organic radicals that are formed upon radiolysis of extraction systems used for practical purposes. Certainly, more extensive studies in this field would be expedient.

Thus, the following general conclusions can be drawn about the reactivity of actinide ions towards inorganic and organic free radicals in aqueous solutions (see also Refs 1, 11–13).

(1) If the ΔE° value of the species involved in reactions occurring by the mechanism of outer-sphere electron transfer is relatively large (~2.3 V and larger), the rates of these reactions are diffusion-controlled or are close to the diffusion limit. However, if the reaction occurs by a complicated mechanism including, for example, complex formation or a structural rearrangement of the actinide ion, this conclusion may be false.

(2) When the reaction rate is not diffusion-controlled, it often depends on the redox potentials of the actinide ions and the radicals participating in the reaction. For example, the reactivity of radicals in oxidation processes changes in the following sequence: $SO_4^- > NO_3 > OH > Cl_2^- > Br_2^- > I_2^- > O_3^-$.

(3) If the structures of actinide ions and free radicals reacting with them are similar, for analogous reactions the rates of which are not diffusion-controlled, the logarithms of rate constants obey a linear correlation with the ΔE° values of the reacting species (see Figs 1 and 2).

Table 15. Rate constants for the reactions of actinides with organic free radicals.

Actinide	Radical	Medium		$10^{-7}k$ (see [a])	Ref.
		I	II		
U(VI)	COOH	H_2SO_4 + HCOOH	1.0 + 5.3	1.0×10^2	88
	COOH	H_2SO_4 + HCOOH	0.4 + 5.3	7.3×10	88
	COOH	H_2SO_4 + HCOOH	0.048 + 5.3	1.0×10^2	88
	COOH	HCOOH	5.3	1.6×10^2	88
	COOH	HCOOH	12.2	1.5×10^2	88
	COOH	HCOOH	17.7	1.3×10^2	88
	COOH	HCOOH	24.4	3.4×10^2	88
	COOH	HCOOH	26.2	5.9×10^2	88
	$(CH_3)_2COH$	H_2SO_4	0.1	2.4×10^2	13
	$(CH_3)_2COH$	–	(~1.0)	4.7	59
	$BpyH_2^+$ (see [b])	$HClO_4$	0.1	9.0	13
	$BpyH_2^+$	H_2SO_4 + HCOOH	1.0 + 5.3	1.1×10	88
	$BpyH_2^+$	H_2SO_4 + HCOOH	0.4 + 5.3	8.6	88
	$BpyH_2^+$	H_2SO_4 + HCOOH	0.048 + 5.3	7.0	88
	$BpyH_2^+$	HCOOH	5.3	6.6	88
	$BpyH_2^+$	HCOOH	12.2	6.0	88
	$BpyH_2^+$	HCOOH	24.4	1.0×10	88
	$PhenH_2^+$ (see [c])	HCOOH	5.3	9.1	88
	$PhenH_2^+$	H_2SO_4 + HCOOH	0.4 + 5.3	1.0×10	88
	$PhenH_2^+$	HCOOH	17.7	8.4	88
	$PhenH_2^+$	HCOOH	26.2	1.0×10	88
	$H.PhenH^+$ (see [d])	$HClO_4$	0.1	$< 2.0 \times 10^{-1}$	89
	R (see [e])	–	(4.0)	9.8	90
U(III)	CH_3 (see [f])	$HClO_4$	0.5	1.5×10^2	45
	CH_2OH	$HClO_4$	0.5	< 2.0	45
	CH_2COOH (see [f])	$HClO_4$	0.5	1.2×10	45
	$(CH_3)_2COH$	$HClO_4$	0.5	< 1.0	45
	$CH_3CHCOOH$ (see [f])	$HClO_4$	0.5	2.1	45
	$CH_2C(CH_3)_2OH$	$HClO_4$	0.5	$< 5.0 \times 10^{-1}$	45
Np(VI)	COOH	HCOOH	12.2	8.7×10^3	88
	COOH	HCOOH	24.4	9.0×10^3	88
	$(CH_3)_2COH$	$HClO_4$	0.1	1.8×10^3	91
	$BpyH_2^+$	$HClO_4$	0.1	8.0×10	91
	$BpyH_2^+$	H_2SO_4 + + HCOOH	0.1 + 2.6	1.9×10^2	88
	$BpyH_2^+$	HCOOH	12.2	1.9×10^2	88
	$BpyH_2^+$	HCOOH	24.4	1.5×10^2	88
	$PhenH_2^+$	$HClO_4$	0.1	5.0×10	91
	$H.PhenH^+$	H_2SO_4	0.1	$\leqslant 3.5 \times 10^{-1}$	91
	R	–	(4.0)	2.27×10^2	90
Pu(VI)	$(CH_3)_2COH$	$HClO_4$	0.1	1.6×10^3	91
	$BpyH_2^+$	$HClO_4$	0.1	1.5×10^2	91
	$PhenH_2^+$	$HClO_4$	0.1	1.3×10^2	91
	R	–	(4.0)	2.26×10^2	90

[a] Expressed in litre $mol^{-1}\,s^{-1}$. [b] From here on, this is the electron adduct of 2,2′-bipyridinium. [c] From here on, this is the electron adduct of *o*-phenanthrolinium. [d] From here on, this is the H-adduct of *o*-phenanthrolinium. [e] From here on, R is the electron adduct of 4,4′-dipropyl-2,2′-bipyridinium. [f] The reaction yields the product of addition of the radical to U(III).

(4) The reactivity of actinide ions is markedly influenced by the formation of complexes. It was noted above that the rate constants for reactions of Np(III) and Pu(III) with the Cl_2^- radical ion increase following an increase in the concentration of chloride ions in the solution. This is due to the formation of inner-sphere chloride complexes possessing a higher reactivity towards Cl_2^- (it has been found that an increase in the concentrations of $HClO_4$, $LiClO_4$ or H_2SO_4 barely influences the rates of the corresponding reactions).

(5) A structural change in the coordination sphere of an actinide ion upon reaction is among the factors having an influence on the reaction rate. For example, this is true for oxidation of An(IV) or reduction of An(V). In these processes, non-oxygenated multi-charged cations are converted into oxygenated cations and *vice versa*. The reactivity can depend on the stability of intermediate ions.

(6) If the rate of the reaction of an actinide ion with a radical ion is not diffusion-controlled, the rate constant depends on the charge of the actinide-containing ion. Among other factors, this may be due to hydrolysis of actinide ions. In some cases, the magnitude of this effect surpasses the influence of the redox potential. This is observed in the reactions of O_2^- with Np(VI) and Np(VII) ions in alkaline media.

IV. Uranium

Radiolytic transformations of uranium ions in aqueous solutions induced by γ- and α-radiation have been studied fairly comprehensively. The main results obtained in these studies are outlined below and are interpreted resorting to the published data on the kinetics of reactions of uranium ions with the products of radiolysis of water and with 'secondary' free radicals.

1. γ-Radiolysis of acidic aqueous solutions of uranium ions

The behaviour of uranium ions in aqueous solutions under the action of X-rays and γ-radiation has been studied; this includes reduction of U(VI) in the presence of acceptors of OH radicals and in the absence of oxygen as well as oxidation of U(III) and U(IV) in deaerated solutions and oxidation of U(IV) in solutions saturated with air.

It is known[1] that when aerated solutions of U(VI) (> 0.2 mol litre^{-1}) in 0.05 M H_2SO_4 are exposed to γ-radiation, the concentration of U(VI) ions does not change and no hydrogen peroxide is detected. This can be explained in the following way: U(VI) is reduced in reactions with e_{aq}^- and H (H is formed not only as a product of water radiolysis but also in the reaction of e_{aq}^- with H^+) to U(V); however, the latter is again oxidised to U(VI) in reactions with OH and H radicals and also with hydrogen peroxide. In neutral and weakly acidic solutions, peroxide complexes of U(VI) are formed; after relatively prolonged irradiation, they precipitate. In sufficiently acidic media, these complexes are soluble, and no precipitate is formed. In solutions saturated with air, U(VI) ions form a complex with the HO_2 radical; disproportionation of this complex yields U(VI) and hydrogen peroxide.

Reduction of U(VI) occurs in solutions containing organic compounds (Table 16).[93,94] In these systems, reactions of H and OH with organic compounds (we denote them by RH_2) are significant. These reactions afford $^{\bullet}RH$ radicals able to reduce U(VI). The U(V) ions resulting from reduction of U(VI) disproportionate to give U(IV) and U(VI). Note that the intermediate formation of U(V) in the radiolytic reduction of U(VI) and oxidation of U(IV) has been confirmed electrochemically.[1]

The formation of one U(IV) ion requires two reducing radicals or two OH radicals. Hydrogen peroxide oxidises U(IV) to U(V) or oxidises U(V) to U(VI), and the OH radical thus formed reacts with RH_2. Therefore, the theoretical reduction yield of U(VI) attained in the case where all the OH radicals are trapped by an organic compound should be $(G_{e_{aq}^-} + G_H + G_{OH})/2 = 3.3$ ion (100 eV)$^{-1}$. [This is valid, provided that $^{\bullet}RH$ reduces U(VI)]. In the presence of *tert*-butyl alcohol, no reduction by an organic radical occurs, because the free radical resulting from the reaction of *tert*-butyl alcohol with OH and H radicals is not a reducing agent (see Table 16). Since in this system hydrated electrons not only reduce U(VI) but also react with H^+ to give H atoms and the latter can partly react with *tert*-butyl alcohol, the reduction yield attained can be found from the following expression:

$$G[-\mathrm{U(VI)}] = G[\mathrm{U(IV)}] < \tfrac{1}{2}(G_{e_{aq}^-} + G_H - G_{H_2O_2}), \quad (3)$$

i.e. $G[-\mathrm{U(VI)}]$ should be smaller than 1.4 ion (100 eV)$^{-1}$.

Table 16. Reduction yields of U(VI) in γ-radiolysis of deaerated solutions of U(VI) containing organic compounds RH_2.[93,94]

RH_2	$[RH_2]$ /M	$G[-(\mathrm{U(VI)}]$ (see [a])	RH_2	$[RH_2]$ /M	$G[-(\mathrm{U(VI)}]$ (see [a])
CH_3OH	0.1	2.6	$(CH_3)_3COH$	0.2	1.0
CH_3OH	0.5	3.0	$(CH_3)_3COH$	0.5	1.1
CH_3OH	1.0	3.0	$(CH_3)_3COH$	0.75	1.3
C_2H_5OH	0.5	3.2	$(CH_3)_3COH$	1.0	1.3
$(CH_3)_2CHOH$	0.5	3.6	HCOOH	0.1	2.3
$(CH_3)_3COH$	0.01	0.7	$H_2C_2O_4$ (see [b])	0.005	0
$(CH_3)_3COH$	0.05	0.8	$H_2C_2O_4$ (see [b])	0.01	0.3
$(CH_3)_3COH$	0.1	0.9	$H_2C_2O_4$ (see [b])	0.1	2.3
			$H_2C_2O_4$ (see [b])	0.3	2.7

[a] Expressed in ion (100 eV)$^{-1}$. [b] Estimated from a figure presented in Ref. 93.

It has been shown[93] that the reduction yield of U(VI) in solutions containing $H_2C_2O_4$ decreases when sulfuric acid is added. This can be explained by the fact that $HC_2O_4^-$, $H_2C_2O_4$ and HSO_4^- compete for OH radicals (the rate constants for the corresponding reactions are commensurable[95]). The two species mentioned first react to give reducing radicals, whereas the reaction with HSO_4^- affords an oxidising radical, which, like the OH radical, is able to oxidise U(IV) and U(V).

When the concentration of organic substances is high, recombination of OH radicals in spurs is partially suppressed, and the reduction yield of U(VI) thus increases.[94]

Reduction of U(VI) also occurs[96] in solutions of nitric acid containing sulfanilamide. The latter reacts with nitrous acid and with NO_3 radicals formed in this system, and this precludes the reverse oxidation of U(V) and U(IV). The reduction yield of U(VI) amounts to 1.3 ion (100 eV)$^{-1}$.

Radiolytic processes in aqueous solutions of U(IV) have also been the objects of several experimental and computer studies.[97] In deaerated solutions of U(IV) in perchloric acid, U(IV) is oxidised to U(VI).[1] The oxidation yield increases as the concentration of U(IV) increases; for [U(IV)] = 0.05 mol litre^{-1} in 0.1 M $HClO_4$, it is 2.45 ion (100 eV)$^{-1}$. At higher concentrations of U(IV), the yield is somewhat lower. In some cases, both $G[-\mathrm{U(IV)}]$ and $G(H_2)$ have been measured. It was found that $G(H_2)$ is much larger than G_{H_2}. The most significant processes in this system are oxidation of U(IV) with OH radicals and with hydrogen peroxide, oxidation of U(V) with H atoms, disproportionation of U(V), reduction of U(IV), U(V) and U(VI) with hydrated electrons and the interaction of U(III) with U(V) and U(VI). With allowance for all these reactions and for the data of Table 1, the $G[-\mathrm{U(IV)}]$ value, which is equal to $G[\mathrm{U(VI)}]$, is 2.3 ion (100 eV)$^{-1}$.

It has been noted[44] that oxidation of U(III) [resulting from the reduction of U(IV) with H atoms] may be ignored in the mechanism of the oxidation of U(IV), because U(III) reacts rapidly with U(V) and U(VI), the concentrations of which are much higher than the steady-state concentration of H atoms. The U(V) ions are long-lived species; therefore their concentration during γ-radiolysis is relatively high.

Vladimirova[97] carried out computer modelling of the radiolysis of deaerated solutions of U(IV) in perchloric acid. Unfortunately, the researcher assumed without proof that the reaction of U(VI) with HO_2 yields U(IV) rather than a complex of U(VI) with HO_2.

When deaerated solutions of U(IV) in aqueous sulfuric acid are exposed to γ-radiation, as in the case of solutions in perchloric acid, U(IV) is oxidised.[1] In a 0.4 M solution of sulfuric acid, the $G[-\mathrm{U(IV)}]$ value increases following an increase in the concen-

tration of U(IV) and is 2.0 – 2.4 ion $(100\ eV)^{-1}$ in the range of its concentrations of 0.02 – 0.05 mol $litre^{-1}$. Upon further increase in the concentration of U(IV), the yield decreases; in a 0.5 mol $litre^{-1}$ solution, $G[-U(IV)]$ is ~ 0.8 ion $(100\ eV)^{-1}$. Evidently, the mechanisms of the radiolysis of solutions containing sulfuric and perchloric acids are similar. In all probability, the decrease in $G[-U(IV)]$ at high concentrations of U(IV) is due to the fact that some of the uranium ions trap the reducing radicals from spurs. Study of radiolytic oxidation of U(IV) has shown that at elevated temperatures, H atoms are also involved in the oxidation, in addition to OH and H_2O_2; therefore, in this case, the oxidation yield is higher than that at room temperature.

γ-Radiolysis of deaerated aqueous solutions of U(IV) in hydrochloric acid has been studied in a number of publications.[1, 57] It was found that the oxidation yield decreases upon an increase in the concentration of HCl and increases following an increase in the concentration of U(IV); however, $G[-U(IV)]$ is much lower than that in solutions containing sulfuric acid.

Oxidation of U(IV) induced by γ-radiation or X-rays in air-saturated solutions in sulfuric acid has been the object of several studies.[1] It was noted that the radiolytic oxidation of U(IV) ions in this system is complicated by their spontaneous oxidation with the atmospheric oxygen. The initial oxidation yields slowly increase when the concentration of U(IV) increases and decrease as the dose rate increases.

Radiolytic oxidation of U(IV) in 0.5 – 3 M HNO_3 saturated with air has been studied.[98] To bind nitrous acid which is able to oxidise U(IV), hydrazine (up to 0.1 mol $litre^{-1}$) was added to the solutions. The oxidation yields were found to decrease with an increase in the concentration of nitric acid. In the presence of U(VI), the yields decrease somewhat. In this system, U(IV) is oxidised by the NO_3 radical (arising in the reaction of OH radicals with nitric acid and NO_3^-), by molecular oxygen and by hydrogen peroxide. The U(VI) introduced into the solution is reduced by intermediate compounds formed in the oxidation of hydrazine; therefore, the oxidation yield of U(IV) diminishes.

A scheme consisting of twenty reactions has been proposed for the mathematical description of radiolytic oxidation of U(IV) in solutions containing nitric acid.[99] The results obtained in terms of this scheme, after selection of unknown rate constants, were apparently in satisfactory agreement with the experimental data.

The oxidation yields of U(IV) during radiolysis of hydrochloric-acid solutions (with a dose rate of 0.39 Gy s^{-1}) saturated with air are lower than those in aerated solutions of sulfuric acid.[1] For example, the maximum yield in air-saturated 0.8 M HCl amounts to 7.8 ion $(100\ eV)^{-1}$.[57]

Trivalent uranium is oxidised during radiolysis in aqueous solutions to give U(IV).[1] Thus its oxidation yield in hydrochloric acid reaches ~ 12 ion $(100\ eV)^{-1}$. If we assume that U(III) is oxidised *via* interaction with H, OH, Cl_2^- and H_2O_2, the calculated oxidation yield is 8.2 ion $(100\ eV)^{-1}$. The experimental value is markedly higher. Perhaps, the solutions were not completely free from oxygen during irradiation.

2. α-Radiolysis of acidic aqueous solutions of uranium ions

Most of the studies dealt with the oxidation of U(IV) in deaerated and aerated aqueous solutions of various acids during α-radiolysis. It has been noted [1] that when solutions of U(VI) in sulfuric acid are exposed to α-particles emitted by radon, uranium is not reduced. When a solution containing both U(IV) and U(VI) has been irradiated by α-particles from radon, U(IV) has been oxidised. In a study of α-radiolysis of deaerated solutions of U(IV) in sulfuric acid, it has been found that the oxidation yield of U(IV) and the yield of formation of molecular hydrogen diminish following an increase in the concentration of U(IV). Uranium(IV) is oxidised by hydrogen peroxide, OH and HO_2 radicals, whereas H atoms (in this medium, they appear instead of hydrated electrons) reduce the resulting U(VI). Thus

$$G[-U(IV)] = \tfrac{1}{2}G_{OH} + G_{H_2O_2} + \tfrac{3}{2} - G_{HO_2} - [G_{H_2} - G(H_2)] - \tfrac{1}{2}(G_{e_{aq}^-} + G_H)\,. \quad (4)$$

For example, the $G[-U(IV)]$ value calculated for a 2×10^{-3} mol-$litre^{-1}$ solution of U(IV) in 1.5 M H_2SO_4 using the primary yields of the products of α-radiolysis of water given in Table 2 is 1.19 ion $(100\ eV)^{-1}$. This value differs somewhat from that found experimentally [1.08 ion $(100\ eV)^{-1}$]. This difference can be due to the fact that the primary yields refer to a 0.4 M solution of sulfuric acid, while the experimental value was measured for 1.5 M H_2SO_4.

The oxidation yield of U(IV) in aerated acidic solutions is markedly higher; it increases with an increase in the concentration of U(IV) and with a decrease in the dose rate.[1] The reactions occurring during α-radiolysis of solutions saturated with air are the same as those occurring during γ-radiolysis. The facts that the oxidation yields induced by α- and γ-radiolyses are high and that they depend on the radiation dose rate indicate that the oxidation of U(IV) follows a chain mechanism.

Study of the influence of the energy of helions (*i.e.* linear transfer of energy) on the $G[U(VI)]$ values for the oxidation of U(IV) in 0.4 M solutions of H_2SO_4 saturated with oxygen or nitrogen has shown that the oxidation yields in oxygen-saturated solutions increase with an increase in the energy of helions, whereas for solutions saturated with nitrogen, the opposite dependence is observed.[100]

Oxidation of U(IV) in 0.2 – 11.5 M solutions of $HClO_4$ exposed to intense α-radiation from ^{244}Cm has been studied.[101] Curium was added to the solution as a solid salt or as its solution. In the former case, the oxidation yield was equal to 1.6 ion $(100\ eV)^{-1}$ in 0.2 – 1 M solutions of $HClO_4$ and increased gradually following an increase in the concentration of the acid; in 10 – 11 M $HClO_4$ the oxidation yield was equal to ~ 6 ion $(100\ eV)^{-1}$ $\{[U(IV)] = 6.6 \times 10^{-3}$ mol $litre^{-1}\}$. It was shown that the yield is almost independent of the dose rate but increases with an increase in the concentration of U(IV). When curium was introduced as a solution, the oxidation yields were 2.7, 7.5 and 50 ion $(100\ eV)^{-1}$ for concentrations of $HClO_4$ of 0.2, 4 and 7 M, respectively. Evidently, the latter value was markedly overestimated. Oxidation of U(IV) occurs *via* the same reactions as it does in solutions containing sulfuric acid. The higher yields attained in this case can be due to the influence of the products of decomposition of $HClO_4$ (ClO_2, Cl_2, ClO_2^-) formed during radiolysis.

It was found [101] that the oxidation yield of U(IV) in nitric-acid solutions during radiolysis induced by α-particles from ^{244}Cm decreases as the content of HNO_3 increases. For concentrations of the acid of 0.5 – 1 and 2 – 8 M, the yields are ~ 2 and ~ 1 ion $(100\ eV)^{-1}$, respectively. When the concentration of HNO_3 is further increased, the yield drops almost to zero. The yields in solutions containing nitric acid are lower than those in solutions of sulfuric and perchloric acids. This is due to the formation of HNO_2, which reacts with H_2O_2 and, possibly, with HO_2.

V. Neptunium

Vast information dealing with radiolytic transformations of neptunium ions in acidic, carbonate-containing and alkaline solutions exposed to γ- and α-radiation can be found in the literature.

1. γ-Radiolysis of acidic aqueous solutions of neptunium ions

γ-Radiolysis of aerated solutions of Np(VI) containing perchloric acid results in accumulation of Np(V); $G[-Np(VI)] = G[Np(V)] = 2.4$ ion $(100\ eV)^{-1}$.[102] The mechanism of this process in a weakly acidic solution includes reactions of Np(VI) with e_{aq}^-, H, HO_2 and H_2O_2 as well as reverse oxidation of Np(V) with OH radicals; the calculated value of $G[-Np(VI)]$ {or $G[Np(V)]$} is 2.3 ion $(100\ eV)^{-1}$. The yield measured in another study [102] coincides with this value. However, earlier publications (they have been considered in a previous monograph [1]) report values

of 4.0 to 6.7 ion $(100\ eV)^{-1}$, depending on the concentrations of Np(VI) and $HClO_4$. Among other reasons, such high yields may be due to the presence of organic impurities in the solutions used. In a 3.4 M solution of $HClO_4$, $G[-Np(VI)]$ was found to be 1.9 ion $(100\ eV)^{-1}$. This low yield can be due to the fact that the reduction of Np(VI) with hydrogen peroxide and HO_2 radicals is retarded and also due to the fact that HO_2 participates to some extent in the oxidation of the resulting Np(V).

The radiolytic behaviour of Np(V) in aerated solutions in perchloric acid has been studied in detail.[102] It was found that Np(V) is fairly stable in these solutions. In particular, in 1 M $HClO_4$, the formation of Np(VI) has been observed only at relatively high radiation doses. In the presence of acceptors that transform hydrated electrons and H atoms into OH radicals, Np(V) is oxidised irreversibly into Np(VI) under the action of γ-irradiation.[102] In solutions with $pH \geqslant 4$, dinitrogen oxide was used as the acceptor. The initial oxidation yield $G[-Np(V)]$, which is equal to $G[Np(VI)]$, was 2.1 ion $(100\ eV)^{-1}$. At $pH \leqslant 1$, xenon trioxide served as the acceptor; it reacted with H to give XeO_2 and OH. It should be noted that in this system, HO_2 radicals and, finally, hydrogen peroxide are also converted into OH radicals. The oxidation yield depends on the concentration of XeO_3; it increases from 6 for 1×10^{-3} mol litre^{-1} of XeO_3 to 13.5 ion $(100\ eV)^{-1}$ for 2×10^{-2} mol litre^{-1} of XeO_3. The mechanism of the radiolytic oxidation of Np(V) in the presence of the acceptors mentioned above has been discussed in Ref. 1.

Radiolytic reduction of Np(VI) and oxidation of Np(IV) in solutions containing sulfuric acid have been studied. Reduction of Np(VI) in these solutions has been described in a number of publications (they are discussed in Ref. 1). The reduction yields range from 4.5–5.0 ion $(100\ eV)^{-1}$ in $\sim 10^{-3}$–10^{-2} M solutions of H_2SO_4 to 2.5–3.0 ion $(100\ eV)^{-1}$ in ~0.4–0.5 M solutions of this acid.

The mechanisms of reduction of Np(VI) in solutions of sulfuric and perchloric acids are similar. The calculated reduction yield in these solutions is 2.3 ion $(100\ eV)^{-1}$. The experimental $G[-Np(VI)]$ values for solutions in sulfuric acid are higher, which is apparently due to the presence of organic impurities.[1]

Reduction of Np(VI) with the heteropoly-blue $PW_{12}O_{40}^{4-}$ in a 0.1 M solution of H_2SO_4 has been studied by pulse radiolysis.[103] The rate constant of the corresponding reaction was measured to be 3.2×10^8 litre mol^{-1} s^{-1}. This is smaller than the diffusion limit rate constants for reactions of oppositely charged ions. The kinetic restrictions during electron transfer are apparently due to the fact that the excess electron is delocalised over the tungsten atoms shielded by the negatively charged oxygen atoms.[104]

Radiolytic oxidation of Np(IV) to Np(V) in aqueous solutions of sulfuric acid has been studied by several researchers (these studies have been surveyed in Ref. 1). In particular, it was found that in aerated solutions the yield increases from ~13 to 15 ion $(100\ eV)^{-1}$ on passing from 1×10^{-2} M to 0.4 M H_2SO_4. Oxidation of Np(IV) in aerated solutions is accomplished *via* reactions with HO_2 (this radical results from interaction of H with O_2), OH and H_2O_2. Therefore, the theoretical value of $G[-Np(IV)]$ is 15.5 ion $(100\ eV)^{-1}$ for 0.4–0.5 M H_2SO_4. This value differs only slightly from the experimental result.

Data on radiolytic processes including reduction of Np(VI) and oxidation of Np(IV) in nitric acid solutions have been reported.

When solutions of Np(VI) in 1×10^{-3}–2 M HNO_3 are exposed to high-energy electrons or to γ-radiation, Np(V) ions are formed.[1,4] The reduction yields decrease with an increase in the concentration of nitric acid or in the dose rate. A peculiar feature of the radiolysis of these solutions is the existence of an induction period at high concentrations of HNO_3.

During γ-radiolysis of aerated solutions of Np(VI) in nitric acid, the following intermediate species are formed: NO_3^{2-} (resulting from the reaction of e_{aq}^- with NO_3^-), HNO_3^- (the reaction of H with NO_3^-) and NO_3 (the reactions of OH with HNO_3 and NO_3^- and direct action of ionising radiation on the nitrate ion). When the concentration of NO_3^- is low, the reaction between H and O_2 is also possible. The OH radical can participate in the oxidation of the Np(V) formed, but at low radiation doses, this process can be neglected. In an acidic medium, the NO_3^{2-} and HNO_3^- radical ions are converted into NO_2; the latter reacts with water to give HNO_2 and NO_3^-. In concentrated solutions of nitric acid, NO_2 and NO_3 radicals can also arise from the direct action of the ionising radiation on HNO_3 and NO_3^-.[6]

The NO_3 radicals oxidise Np(V) and undergo dimerisation or hydrolysis. Hydrolysis yields NO_2 and hydrogen peroxide. The dimer N_2O_6 can reduce Np(VI).[1] The dimerisation of NO_3 radicals is fairly significant in concentrated solutions of HNO_3 in which these radicals are formed in a high yield upon interaction of NO_3^- and HNO_3 with OH and also upon direct action of the ionising radiation on the solute. In addition, trapping of reducing radicals by nitrate ions in spurs should also be taken into account. Nitrous acid reduces Np(VI) and destroys hydrogen peroxide. As the concentration of H^+ increases, the rate of the reaction of this acid with Np(VI) decreases, while the rate of the reaction with hydrogen peroxide increases.

Reduction of Np(VI) in aerated 1×10^{-3}–5×10^{-2} M solutions of HNO_3 occurs *via* its reactions with the HO_2 radical, hydrogen peroxide and nitrous acid. The reaction between HNO_2 and H_2O_2 in these solutions can be ignored. The resulting Np(V) is oxidised by the NO_3 and OH radicals. When the concentration of HNO_3 is 1 M or higher, the mechanism of radiolytic transformations becomes somewhat different. Firstly, hydrogen atoms are consumed in the reactions with NO_3^-, whereas the reaction between H and O_2 plays only a minor role; secondly, the rates of reactions of Np(VI) with HO_2 and HNO_2 decrease; thirdly, the reaction between HNO_2 and H_2O_2 accelerates; fourthly, Np(V) is reduced by nitrous acid. A decrease in the dose rate results in a decrease in the concentrations of H_2O_2 and HNO_2; hence, the rate of the reaction between these species decreases, and the proportions of H_2O_2 and HNO_2 that react with Np(VI) increase.

The existence of an 'induction period' in concentrated solutions of HNO_3 can be explained by the fact that the reaction between Np(VI) and hydrogen peroxide in these systems occurs slowly, and Np(V) appears only after accumulation of a fairly large amount of HNO_2 in the solution.

The influence of U(VI) on the radiolytic reduction of Np(VI) in solutions of nitric acid has been studied.[1] An increase in the concentration of U(VI) leads to an increase in the yield of Np(V). It was postulated that a cation–cation complex formed by U(VI) and Np(V) plays an important role in this process. However, later it has been shown [105] that the radiolytic transformations in this system can be interpreted without invoking the idea of cation–cation interactions. It was noted [1] that the introduction of Ce(IV) (up to ~2×10^{-2} mol litre^{-1}) exerts no influence on the yield of Np(V).

On exposure to γ-radiation, Np(IV) ions in aerated and deaerated solutions of nitric acid are oxidised to Np(V) (for concentrations of HNO_3 ranging from 1×10^{-3} to 0.5 M) and to Np(VI).[1,106] The oxidation yield of Np(IV) in aerated solutions depends on the concentration of nitric acid: initially, it increases from 7 to 9 ion $(100\ eV)^{-1}$ following an increase in the $[HNO_3]$ value from 5×10^{-3} to 0.1 M, and then it decreases to 1.5 to 2.6 ion $(100\ eV)^{-1}$ for $[HNO_3] = 1$–6 M. In the case of deaerated solutions, this yield is almost constant, 4.0 to 4.6 ion $(100\ eV)^{-1}$ ($[HNO_3] = 5 \times 10^{-3}$–0.4 M).[1,106]

During γ-radiolysis of deaerated solutions, NO_2, NO_3 and HNO_2 are formed; Np(IV) reacts with OH, HO_2, H_2O_2 and e_{aq}^-, and Np(III) reacts with Np(V). The role of the reaction between HNO_2 and H_2O_2 is relatively small. The formation of NO_3 under the action of ionising radiation can be neglected at $[HNO_3] \leqslant 0.4$ M. It is assumed that HNO_2 does not react with Np(IV). For concentrations of HNO_3 equal to 0.1 and 0.4 M, the reaction of Np(IV) with e_{aq}^- and, hence, the reaction between Np(III) and Np(V) can be ignored. For these solutions

$$G[-Np(IV)] = G_{OH} + 2G_{H_2O_2} = 4.55 \text{ ion } (100\ eV)^{-1}.$$

The experimental $G[-Np(IV)]$ values found for the above concentrations of HNO_3 are close to this value. The fact that at

low concentrations of HNO_3, the $G[-Np(IV)]$ values are smaller is due to the occurrence of the reactions between Np(IV) and e_{aq}^- and between Np(III) and Np(V).

In 5×10^{-3}–0.5 M solutions of HNO_3 saturated with air, the oxidation yield of Np(IV) should be higher than that in deaerated solutions, since the former contain HO_2 radicals (resulting from the reaction of H with O_2) able to oxidise Np(IV). In aerated 1 to 6 M solutions of HNO_3, the reaction with HO_2 is insignificant, H_2O_2 reacts completely with HNO_2, and the OH radicals are consumed to give NO_3. The yield of NO_3 is larger than G_{OH} owing to the direct action of the ionising radiation on NO_3^- and HNO_3. However, $G[-Np(IV)] < G_{OH}$. This is apparently due to the fact that not all the NO_3 radicals are consumed in the reaction with Np(IV); some of these radicals can be hydrolysed and involved in the oxidation of nitrous acid. A decrease in the concentration of Np(IV) is favourable for the side reactions of NO_3.

According to Rotmanov *et al.*,[107] prolonged irradiation of solutions of tetravalent neptunium in aqueous nitric acid results in the establishment of steady-state (equilibrium, as the researchers state) concentrations of HNO_2, Np(IV), Np(V) and Np(VI). For example, when the initial concentrations of Np(IV) and HNO_3 are 3×10^{-3} and 1 mol litre^{-1}, the steady-state concentrations are the following: 7.5×10^{-5} mol litre^{-1} (HNO_2) and 3%, 92% and 5% [Np(IV), Np(V) and Np(VI), respectively]. In the case where the concentrations of Np(IV) and HNO_3 are 3×10^{-3} and 6 mol litre^{-1}, the steady-state concentrations are equal to 1.6×10^{-4} mol litre^{-1} and 36%, 40% and 24%, respectively. It can be seen that as the concentration of nitric acid increases, the steady-state concentrations of Np(IV) and Np(VI) increase. This is due to the reaction between Np(VI) and HNO_2 and to disproportionation of Np(V).

2. α-Radiolysis of acidic aqueous solutions of neptunium ions

α-Radiolysis of tetravalent and hexavalent neptunium has been studied in solutions containing perchloric and nitric acids. Under the action of its own α-radiation, Np(VI) ions in 0.48–1.7 M solutions of $HClO_4$ are converted into Np(V).[1] The rate constant for the reduction in 0.044–0.3 M solutions of Np(VI) is 3.1×10^{-9} s^{-1}. Using this value, the half-life period of ^{237}Np (2.2×10^6 years) and the energy of α-particles (4.8 MeV), G[Np(V)] was found to be 6.4 ion (100 eV)$^{-1}$.

The processes occurring during α-radiolysis are the same as those occurring during γ-radiolysis. The theoretical reduction yield [achieved when the reducing radicals, precursors of H_2, are completely trapped from spurs by Np(VI)] is 5.8 or 6.5 ion (100 eV)$^{-1}$, depending on which $G_{H_2O_2}$ value (from Table 2 or from Ref. 108) has been used for calculations.

Reduction of Np(VI) (present in a concentration of 1.5×10^{-3} to 1×10^{-2} mol litre^{-1}) in solutions of perchloric acid induced by the α-radiation from ^{244}Cm has been studied.[108] It was shown that owing to the low content of Np(VI) and to the high acidity, the reaction of Np(VI) with H_2O_2 occurs slowly; therefore, it does not come to an end at the instant when the concentrations of Np(VI) and Np(V) are measured. For example, for a solution containing 1.5×10^{-3} mol litre^{-1} of Np(VI) and 1.0 mol litre^{-1} of $HClO_4$ (and for a dose rate of 2.25 Gy s^{-1}), the reduction yields found at the moment of measurement and after the completion of the reaction are 1.6 and 3.5 ion (100 eV)$^{-1}$, respectively.

Under the action of α-particles, Np(IV) in aerated solutions of perchloric acid is oxidised to Np(V) {at $[HClO_4] < 1$ M} or to Np(VI) {at $[HClO_4] > 1$ M}.[107] The oxidation yields are 0.8 to 1.8 ion (100 eV)$^{-1}$ depending on the concentrations of the acid and Np(IV).

During α-radiolysis of aerated solutions of Np(IV) in which $[HClO_4] < 1$ M, H reacts with O_2, Np(IV) reacts with OH, HO_2, H_2O_2 and e_{aq}^- and Np(III) reacts with Np(V). The partial trapping of reducing radicals in the spurs by Np(IV) ions (their concentration is fairly high) should also be taken into account. Therefore, the yield of Np(IV) can be found from the equation:

$$G[-Np(IV)] = 3(G_H + G_{HO_2}) + G_{OH} + 2G_{H_2O_2} - G_{e_{aq}^-} - 2QG_{H_2}, \quad (5)$$

where Q is a coefficient characterising the proportion of reducing radicals trapped by Np(IV) ions in the spurs.

The minimum oxidation yield should be obtained when the reducing radicals in the spurs are completely trapped by Np(IV) ions. This is equal to ~0.9–1.2 ion (100 eV)$^{-1}$.

When solutions of Np(V) in 4–6 M $HClO_4$ are exposed to α-radiation, an 'induction period' is observed;[107] during this period, Np(VI) ions do not appear but small amounts of Np(IV) are formed.

The transformations of Np(IV) and Np(VI) ions induced by α-radiation in solutions of nitric acid have been studied repeatedly.[1,4] Both Np(IV) and Np(VI) are converted into Np(V) under the action of α-particles. The yields attained in these processes are listed in Table 17.

The reduction yield of Np(VI) during α-radiolysis of its solutions containing nitric acid is basically determined by the same reactions as in the case of γ-radiolysis. The calculated yield

Table 17. The reduction yields of Np(VI) and oxidation of Np(IV) in α-radiolysis of aerated nitric-acid solutions of neptunium (concentration of neptunium ~10^{-3} mol litre^{-1}).[1,4]

$[HNO_3]$ /M	G /ion (100 eV)$^{-1}$	$[HNO_3]$ /M	G /ion (100 eV)$^{-1}$
Reduction, dose rate 2.7×10^{-3}		Oxidation, dose rate 2.7×10^{-2}	
1.0×10^{-3}	3.0–3.2	5.0×10^{-3}	2.3
1.0×10^{-2}	5.0	1.0×10^{-2}	2.6
0.1	6.0	5.0×10^{-2}	3.0
0.5	6.6 [a]	0.1	3.4
1.0	5.7 [a]	0.3	3.8
2.0–2.1	4.2	0.5	4.2
		1.0	4.0

[a] For these data no dose rate is given in Ref. 4.

for a 1×10^{-3} M solution of HNO_3 amounts to 3.4 ion (100 eV)$^{-1}$, which is close to the experimental value.[1] When the concentration of HNO_3 is increased to ~0.5 M, the $G[-Np(VI)]$ value increases to 6.6 ion (100 eV)$^{-1}$. This is due to the fact that the nitrate ions suppress the formation of H_2 in the spurs. When this process is suppressed completely, $G[-Np(VI)]$ should be equal to 6.2 ion (100 eV)$^{-1}$. The reasons for the decrease in the yield at $[HNO_3] \geqslant 1$ M are the same as in the case of γ-radiolysis.

Oxidation of Np(IV) in a 1×10^{-3} M solution of HNO_3 should proceed *via* its reactions with OH, HO_2 and H_2O_2. Besides, Np(IV) ions can be reduced by the radicals (precursors of H_2) that they trap in the spurs. As the concentration of HNO_3 increases, nitrate ions trap more and more reducing radicals in the spurs; therefore, the yield should decrease. However, owing to the low dose rate, the reaction between HNO_2 and hydrogen peroxide occurs slowly; H_2O_2 is mostly consumed for oxidation of Np(IV), and thus the yield of the process increases.

Study of the behaviour of neptunium ions in solutions of nitric acid exposed to larger dose rates of α-radiation created by ^{244}Cm has shown[109,110] that in 0.11 M HNO_3, Np(VI) is totally reduced to Np(V); however at higher concentrations of the acid (0.33 and 0.62 M), steady states are established, both Np(VI) and Np(V) being present in the solution. In a 1.1 M solution of HNO_3 and at a radiation dose of 30–40 kGy, Np(IV) appears. When the dose rate or the concentration of the acid increases, the content of Np(IV) also increases. An increase in the dose rate results in a decrease in the reduction yield. For example, in a solution containing 0.62 mol litre^{-1} of HNO_3 and 2.3×10^{-3} mol litre^{-1} of Np(VI), $G[-Np(VI)]$ diminishes from 3.5 to 2.2 ion (100 eV)$^{-1}$ as the dose rate increases from 1.65 to 4.56 Gy s^{-1}; evidently, this is due to the reaction between HNO_2 and H_2O_2.[109]

On exposure to the same type of radiation, Np(IV) is oxidised to give Np(V) and Np(VI). When the radiation dose is sufficiently large, Np(IV) in solutions with $[HNO_3] < 1$ M is totally oxidised

yielding Np(V) (80% – 95%) and Np(VI).[109] The oxidation yield diminishes following an increase in the dose rate. Thus in a solution containing 0.75 mol litre^{-1} of HNO_3 and $\sim 2 \times 10^{-3}$ mol litre^{-1} of Np(IV), the $G[-\mathrm{Np(IV)}]$ value diminishes from 1.4 to 0.4 ion (100 eV)$^{-1}$ as the dose rate increases from 0.65 to 4.9 Gy s^{-1}. This is caused by acceleration of the reaction between HNO_2 and H_2O_2. In solutions with $[HNO_3] > 1$ M, steady states for Np(IV), Np(V) and Np(VI) are established. As the concentration of the acid increases, the proportions of Np(IV) and Np(VI) increase, while that of Np(V) decreases.[112]

The possibility of computer modelling of the changes in the oxidation states of neptunium ions during α- and γ-radiolysis in solutions in nitric acid has been shown.[111–116] A scheme consisting of 26 reactions was composed; with the use of experimental radiation-chemical yields and the known rate constants for some reactions, this scheme made it possible to describe adequately the radiolytic oxidation of Np(IV) and Np(V) and also the reduction of Np(VI) and Np(V) in 1 – 6 M solutions of HNO_3.

Measurement of the solubility of Np(IV) and Np(V) hydroxides in a 5.3 M solution of NaCl has shown that upon prolonged storage of this system, the solubility of Np(IV) hydroxide increases with time, owing to α-radiolysis.[117] The solubility of the samples of Np(IV) and Np(V) hydroxides was found to be $10^{-5} – 10^{-6}$ M at pH 8 – 13.

3. γ-Radiolysis of alkaline aqueous solutions of neptunium ions

The development of a radiolytic method for the preparation of heptavalent neptunium, plutonium and americium is an important achievement in the radiation chemistry of aqueous solutions. Heptavalent actinides are formed upon irradiation of alkaline solutions of hexavalent actinide ions in the presence of acceptors of hydrated electrons.

The radiolytic method for the preparation of Np(VII) was developed by Pikaev *et al.*[118,119] It consists in the γ-irradiation of an alkaline (in 1 M NaOH) solution of Np(VI) (2×10^{-4} mol litre^{-1}) saturated with N_2O. Dinitrogen oxide reacts with e^-_{aq} to give O^- radical ions. In the absence of N_2O, the hydrated electron reduces the Np(VII) formed and reacts with Np(VI). Apart from N_2O, $S_2O_8^{2-}$, $H_3IO_6^{2-}$, BrO^- and BrO_4^- ions have also been used as scavengers for hydrated electrons. The characteristic features of the method, the yields of Np(VII) under various experimental conditions and the mechanism of oxidation have been considered in detail previously.[1]

The rate constant for the reaction of Np(VII) with Np(V) has been estimated by pulse radiolysis.[54] It is equal to $\sim 2 \times 10^7$ litre mol^{-1} s^{-1} in 0.033 – 2.0 M solutions of LiOH. In solutions of NaOH, this reaction occurs more slowly.

When hydrogencarbonate or carbonate solutions of Np(VI) (2×10^{-4} mol litre^{-1}) saturated with N_2O or solutions containing 0.1 mol litre^{-1} of $K_2S_2O_8$ are subjected to γ-radiolysis, no Np(VII) is formed.[53] A slight quantity of Np(VII) arises in a 0.5 M solution of Na_2CO_3 containing 0.01 mol litre^{-1} of NaOH. An increase in the concentration of NaOH to 0.02 mol litre^{-1} results in the accumulation of 3×10^{-5} mol litre^{-1} of Np(VII); in a 0.03 M solution of NaOH, almost all the Np(VI) is converted into Np(VII). In this case, the formation of Np(VII) in the presence of N_2O occurs without any 'induction period', Np(VI) being completely converted into Np(VII) at a radiation dose of ~600 Gy. The yield of Np(VII) increases from 0.7 to 4.8 ion (100 eV)$^{-1}$ following an increase in the concentration of NaOH from 0.02 to 0.1 M, and then somewhat decreases {to 4.1 ion (100 eV)$^{-1}$ at [NaOH] = 1 M}. Obviously, the reaction of Np(VI) with CO_3^- plays an important role in these systems.

Neptunium(VI) is not oxidised in carbonate-containing solutions. This can be explained by the high redox potential of the Np(VII)/Np(VI) pair and also by the fact that Np(VI) exists as $NpO_2(CO_3)_3^{4-}$ under these conditions.[53] When the solution is alkalified, $(NpO_4 \cdot nH_2O)^{2-}$ ions appear in it, and they react with CO_3^- radical ions. Apparently, the oxidation process consists in the transfer of an electron from Np(VI) to CO_3^-.

Irradiation of aerated alkaline solutions of Np(VII) gives rise to Np(VI) ions.[1] If the radiation rate is larger than 300 Gy and [NaOH] = 0.5 – 1 M, the reduction yield is 2.2 to 2.4 ion (100 eV)$^{-1}$. This is in agreement with the calculated value, which is equal to 2.2 ion (100 eV)$^{-1}$.

Reduction of Np(VI) and Np(V) in aerated alkaline solutions under the action of γ-radiation of ^{60}Co has been studied.[120,121] It was found that Np(VI) is reduced to Np(V) and then to Np(IV). The reduction yield hardly depends on the concentration of alkali over the range of concentrations studied (0.9 to 8.5 mol litre^{-1}) and amounts to 1.4 – 1.6 ion (100 eV)$^{-1}$ (for radiation doses smaller than 650 Gy). However, the yield diminishes upon an increase in the dose.

The yield markedly increases in the presence of organic substances acting as acceptors of O^- radical ions. In a 2 M solution of NaOH containing 0.013 mol litre^{-1} of ethylenediaminetetraacetate ions, the yield is 8.5 ion (100 eV)$^{-1}$ (for a dose of 109 Gy). If the solution contains 1.5 mol litre^{-1} of NaOH and 0.26 mol litre^{-1} of formate ions, $G[-\mathrm{Np(VI)}] =$ 5.8 ion (100 eV)$^{-1}$ (for doses of $\leqslant$ 250 Gy). When carbonate ions are introduced in the solution, the yield barely changes. No reduction of Np(VI) is observed in the presence of nitrite or nitrate ions under low radiation doses (up to 2 – 3 kGy). However, when the doses are relatively high (more than 10 kGy), a peroxo-complex of Np(V) is formed in solutions containing NO_3^-.[63,120,121]

Irradiation of aerated alkaline solutions of Np(V) results in the formation of Np(IV) as the corresponding hydroxide, which precipitates from the solution.

It should be noted that γ-radiolysis of alkaline aqueous solutions of Np(V), Np(VI) or their mixtures is accompanied by specific oscillations.[120–122] They are manifested as a periodical variation of the optical density of the solution. Initially (at low doses), the opical density decreases owing to radiolytic reduction, and then increases due to the light scattering caused by the formation of a finely dispersed suspension. When the irradiated solution is allowed to stand for several hours, the suspension coagulates to give a precipitate, and the optical density decreases. Repeated irradiation results again in the formation of a finely dispersed suspension, and the optical density thus increases. These oscillations of the optical density can be observed until neptunium is entirely reduced to Np(IV).

The mechanism of reduction includes reactions of neptunium ions with e^-_{aq}, O_2^-, and HO_2^- and partial reverse oxidation of the reduced ions with O^- and O_3^- radicals. Based on this mechanism, the following equations were obtained:[120,121]

$$G[-\mathrm{Np(VI)}] = G[\mathrm{Np(V)}] = G_{e^-_{aq}} + G_H + 2G_{H_2O_2} - G_{OH}\,, \qquad (6)$$

$$G[-\mathrm{Np(VI)}] = G[\mathrm{Np(IV)}] = \tfrac{1}{2}(G_{e^-_{aq}} + G_H + 2G_{H_2O_2} - G_{OH}). \qquad (7)$$

In all probability, Eqn. (6) is valid for the reduction of Np(VI) to Np(V), while Eqn. (7) holds for the reduction of Np(VI) to Np(IV).

For solutions containing 1 mol litre^{-1} of an alkali, the yields of the products of water radiolysis at pH 12 – 13 (see Table 1) can be used to calculate the reduction yields from Eqns (6) and (7). In this case, these yields amount to 2.2 ion (100 eV)$^{-1}$ [for the reduction to Np(V)] and 1.1 ion (100 eV)$^{-1}$ [for the reduction to Np(IV)]. The value of 1.4 – 1.6 ion (100 eV)$^{-1}$ given above for doses below 650 Gy indicates that at these doses, both Np(V) and Np(IV) are produced.

The increase in the reduction yields for solutions containing ethylenediaminetetraacetate or formate ions is due to the interaction of these substances with the O^- radical ions to give organic radicals that act as reducing agents and reduce an additional amount of Np(VI). For these systems, Eqns. (6) and (7) are transformed into the following expressions:

$$G[-\mathrm{Np(VI)}] = G[\mathrm{Np(V)}] = G_{e^-_{aq}} + G_H + G_{OH} + 2G_{H_2O_2}\,, \qquad (8)$$

$$G[-\mathrm{Np(VI)}] = G[\mathrm{Np(IV)}] = \tfrac{1}{2}(G_{e^-_{aq}} + G_H + G_{OH} + 2G_{H_2O_2})\,. \qquad (9)$$

The substitution of the numerical values should give the yields equal to 8.0 [for the reduction to Np(V)] and 4.0 ion $(100\ eV)^{-1}$ [for the reduction to Np(IV)]. The value found experimentally for a solution containing ethylenediaminetetraacetate is close to that calculated from Eqn. (8); thus, at low radiation doses, Np(VI) in this system is reduced only to Np(V). The yield found for a solution containing formate ions [5.8 ion $(100\ eV)^{-1}$ for doses below 250 Gy] implies that in this case, Np(VI) is reduced to give both Np(V) and Np(IV).[120, 121]

The formation of a peroxo-complex of Np(V) in solutions containing nitrate ions is due to the fact that the products of radiolytic transformations of NO_3^- protect the arising Np(V) from reverse oxidation (with O^- and O_3^- radical ions) to Np(VI) and from its subsequent reduction to Np(IV) [apparently, the product of reaction between NO_3^- and e_{aq}^- is not able to reduce Np(VI)].[63] Thus, after a sufficient quantity of Np(V) has been accumulated and the greater part of Np(VI) has been consumed, the possibility for the interaction of Np(V) with H_2O_2 appears.

The reduction of Np(V) in aerated alkaline solutions occurs *via* its reaction with hydrated electrons. Since Np(IV) is poorly soluble in alkali and precipitates from alkaline solutions, its reverse oxidation with O^- and O_3^- radical ions proceeds at a slow rate, if at all. Hydrated electrons also react with oxygen in this system; however, O_2^- (and obviously HO_2^-) are unable to reduce Np(V). The O^- and O_3^- radical ions partially oxidise Np(V) to Np(VI) and also react with hydrogen peroxide and with O_2^-.

VI. Plutonium

Transformations of plutonium ions in solutions of mineral acids induced by X-ray-, γ- and α-radiations have been studied by many researchers. The interest in these processes is caused by the fact that, after dissolution, plutonium reacts with the products of radiolysis of the solvent (water and acids) resulting from the action of the radiation of fission-product elements and actinides. The fact that the redox potentials for pairs of plutonium ions in various oxidation states are close to one another accounts for their simultaneous existence in solutions. This fact should be taken into account during isolation, purification and preparation of plutonium compounds.

1. γ-Radiolysis of acidic aqueous solutions of plutonium ions

Radiolytic transformations of plutonium ions induced by X-ray or γ-radiation and high-energy electrons have been studied in solutions of various acids. Radiolysis has been investigated for solutions of Pu(VI), Pu(IV) and Pu(III), solutions containing plutonium in several oxidation states and solutions containing plutonium together with uranium.

In a study [123] (see also Ref. 1) of the behaviour of Pu(VI) ions in 0.2–0.5 M solutions of $HClO_4$ under the action of γ-radiation from ^{60}Co, it has been found that for solutions containing 4.3×10^{-3} mol litre^{-1} of Pu(IV) and 0.2 mol litre^{-1} of $HClO_4$, the reduction yield immediately after irradiation (with a dose of ~7.5 kGy) amounted to 0.8 ion $(100\ eV)^{-1}$; this corresponds to the following equation:

$$G[-\mathrm{Pu(VI)}] = G_{e_{aq}^-} + G_H - G_{OH}\ .$$

Twenty four hours later the reduction yield in the same solutions was 2.3 ion $(100\ eV)^{-1}$. The theoretical yield is equal to:

$$G[-\mathrm{Pu(VI)}] = G_{e_{aq}^-} + G_H + 2G_{H_2O_2} - G_{OH}\ .$$

Ten days after irradiation the yield was 1.2 ion $(100\ eV)^{-1}$. The equation for the theoretical yield is the following:

$$G[-\mathrm{Pu(VI)}] = \tfrac{1}{2}(G_{e_{aq}^-} + G_H + 2G_{H_2O_2} - G_{OH})\ .$$

The dissimilar reduction yields measured within various periods after irradiation are due to the occurrence or absence of the reaction of Pu(VI) with H_2O_2 and to disproportionation of the Pu(V) formed. It should be noted that when the radiation dose is high and the solution is kept after irradiation for a long period, Pu(III) appears. This is due to the reaction between Pu(IV) and Pu(V) and also, possibly, to the reduction of Pu(IV) with hydrogen peroxide (*via* the formation of a peroxide complex). The results of the γ-radiolysis of deaerated solutions of Pu(VI) are similar to those obtained for aerated solutions.

During the γ-radiolysis of solutions of Pu(III) in 0.2 and 0.5 M $HClO_4$, no plutonium ions in other oxidation states are accumulated.[1, 123] In these solutions, oxidation of Pu(III) and reduction of Pu(IV) completely counterbalance each other.

When aerated solutions of 4×10^{-3} mol litre^{-1} of Pu(IV) and 1×10^{-3} mol litre^{-1} of Pu(III) in 0.2 and 0.5 M $HClO_4$ are exposed to γ-radiation, Pu(III) is accumulated.[1, 123] The Pu(IV) ions are reduced by H atoms, e_{aq}^-, HO_2 and H_2O_2 (*via* the intermediate formation of a peroxide complex). The OH radicals participate in the oxidation of Pu(IV).

When a solution containing 3.6×10^{-4} mol litre^{-1} of plutonium in 0.3 M $HClO_4$ (and apparently saturated with nitrogen) has been exposed to X-ray radiation, only oxidised [Pu(V) and Pu(VI)] and reduced [Pu(III) and Pu(IV)] forms of plutonium ions have been distinguished.[1] Under the action of this kind of radiation, plutonium can be reduced or oxidised depending on the ratio of the oxidised and reduced forms in the initial solution. In solutions containing plutonium and uranium, both reduction and oxidation of plutonium ions occur. The yield and the degree of reduction increase with an increase in the concentration of U(VI), the process occuring at the expense of U(V).

The behaviour of plutonium ions in solutions containing sulfuric acid is markedly influenced by the formation of complexes with sulfate ions. This process results in a decrease of the formal redox potentials of the Pu(VI)/Pu(V) and Pu(IV)/Pu(III) pairs; therefore, hydrogen peroxide no longer reduces Pu(IV) but, instead, it mostly oxidises Pu(III). In this case, disproportionation of Pu(V) occurs more rapidly.

The results concerning the radiolytic reduction of Pu(VI) in solutions of sulfuric acid and obtained in a number of studies have been discussed in the previous monograph.[1] The reduction yields vary from 1.2 to 2.5 ion $(100\ eV)^{-1}$ depending on the concentrations of Pu(VI) and sulfuric acid and also on the dose rate. The yields decrease with an increase in the concentration of sulfuric acid or sulfate ions and with a decrease in the concentration of Pu(VI). The mechanism of radiolytic transformations is identical to that for solutions in perchloric acid.

During γ-radiolysis of both aerated and deaerated 1×10^{-3} mol litre^{-1} solutions of Pu(III) in 0.4 M H_2SO_4, Pu(III) is oxidised to Pu(IV).[1] In the case of aerated solutions, post-radiation slow oxidation of Pu(III) with the hydrogen peroxide resulting from radiolysis is observed. The initial yields of Pu(IV) and H_2O_2 are 6.6 ion $(100\ eV)^{-1}$ and 4.0 molecule $(100\ eV)^{-1}$, respectively; this is in agreement with the calculated values. In deaerated solutions containing 10^{-4}–10^{-3} mol litre^{-1} of Pu(III), the yields of Pu(IV) and H_2 are 5.5 and 3.6 molecule $(100\ eV)^{-1}$.

In 0.2 M HCl, hexavalent plutonium is reduced to pentavalent plutonium.[123] When the radiation dose is ~29 kGy, the reduction yield amounts to 0.56 equivalents $(100\ eV)^{-1}$. The resulting Pu(V) disproportionates to give Pu(IV) and Pu(VI). The yield attained in a 0.5 M solution of HCl is somewhat lower. In hydrochloric acid, OH radicals are consumed, and Cl_2^- radical ions arise instead. The latter participate in the oxidation of Pu(V). Trapping of OH radicals or their precursors from the spurs by chloride ions decreases $G_{H_2O_2}$, increases G_{OH} and decreases $G[-\mathrm{Pu(VI)}]$. Irradiation of a 4×10^{-3} mol litre^{-1} solution of Pu(III) in 0.5 M HCl gives rise to Pu(IV), which is formed as a peroxide complex or as a polymer. Radiolytic oxidation of Pu(III) to Pu(IV) in a deaerated 0.8 M solution of HCl during γ-radiolysis occurs with a yield of 4–5 ion $(100\ eV)^{-1}$ at a radiation dose of ~1 kGy or 0.7 ion $(100\ eV)^{-1}$ when the radiation dose is above 3.8 kGy.[1] The oxidation yield of Pu(III) in aerated solutions of hydrochloric acid also decreases following an increase in the dose, which is due to consumption of oxygen and also to reverse reduction of Pu(IV).

Radiolysis of solutions of Pu(III) in hydrochloric acid has been studied under various conditions.[124] It was found that in a deaerated solution containing 0.8 mol litre^{-1} of HCl and 1×10^{-3} mol litre^{-1} of Pu(III), the initial values of G[Pu(IV)] and $G(H_2O_2)$ are 5.0 ion (100 eV)$^{-1}$ and 0.6 molecule (100 eV)$^{-1}$, respectively. The yield increases somewhat when [Pu(III)] = 10^{-2} mol litre^{-1}. When the radiation doses are 3–5 kGy, a steady state is established, *i.e.* the ratio of the concentrations of Pu(III) and Pu(IV) remains constant. Irradiation of a 1×10^{-3} mol litre^{-1} solution of Pu(IV) results in the appearance of Pu(III), the initial yields of Pu(III) and H_2O_2 being equal to 0.36 ion (100 eV)$^{-1}$ and 0.18 molecules (100 eV)$^{-1}$, respectively. When a solution containing 4.9×10^{-4} mol litre^{-1} of Pu(III) and 5.2×10^{-4} mol litre^{-1} of Pu(IV) is exposed to γ-radiation, Pu(III) is oxidised to only a small extent, whereas $G(H_2O_2)$ is equal to 0.46 to 0.83 molecule (100 eV)$^{-1}$.

In a solution of Pu(III) in 0.8 M HCl saturated with oxygen, the yields of Pu(IV) and H_2O_2 are 6.5 ion (100 eV)$^{-1}$ and 4.0 molecule (100 eV)$^{-1}$, respectively (they do not depend on the radiation dose up to ~1 kGy).[124] When the dose is ~2 kGy, the system remains unchanged, while at 4.5 kGy, a peroxide complex of Pu(IV) is formed.[124] In 9 M HCl saturated with oxygen, Pu(III) is oxidised with an initial yield of 8.2 ion (100 eV)$^{-1}$.

The majority of studies dealing with the radiation chemistry of aqueous solutions of plutonium are devoted to the radiolysis of its solutions in nitric acid. This is due to the fact that systems containing nitric acid are often used in the processing of irradiated nuclear fuel.

Study of the γ-radiolysis of solutions of Pu(VI) and mixtures of Pu(IV) and Pu(VI) in 0.5 and 1.5 M solutions of HNO_3 has shown that in solutions containing 3×10^{-3}, 5×10^{-3} and 1×10^{-2} mol litre^{-1} of plutonium, Pu(VI) is not reduced (for radiation doses of up to ~29 kGy). The results obtained by other researchers are somewhat different (see Ref. 1). It was found that when 2×10^{-4}–2×10^{-3} mol litre^{-1} solutions of Pu(VI) in 0.001–0.5 M HNO_3 are exposed to γ-radiation, Pu(VI) is consumed. The reduction yields were found to decrease with an increase in the dose rate and in the concentration of HNO_3. An important role in the systems under consideration belongs to the formation of nitrous acid (upon the reduction of HNO_3 and NO_3^- with H atoms and e_{aq}^-) and its subsequent reactions with Pu(VI) and H_2O_2 as well as to the reverse oxidation of the resulting Pu(V) with NO_3 radicals. The mechanism of radiolysis of nitric acid solutions of Pu(VI) under these conditions has been discussed in detail previously.[1] The influence of the reaction conditions on the reduction yield of Pu(VI) was also considered in the monograph cited. The authors obtained equations describing the dependence of $G[-\text{Pu(VI)}]$ on the dose rate and on the concentration of Pu(VI).

The character of the reduction of Pu(VI) in 0.3–8 M (at a dose rate of 2.67 Gy s^{-1}) depends on its concentration.[125, 126] When $[\text{Pu(VI)}]_0 = 5\times10^{-3}$ mol litre^{-1}, no reduction occurs in the above range of concentrations of HNO_3 up to a dose of 2.4 MGy. When $[\text{Pu(VI)}]_0 = 0.1$ mol litre^{-1}, Pu(VI) is reduced to Pu(IV) in 0.3–4 M HNO_3 and is not reduced in 8 M HNO_3 (at a dose of 2.4 MGy). In 0.3–1.0 M solutions of HNO_3, reduction starts immediately after the beginning of irradiation, whereas in the case of 3–4 M solutions, the process starts after an induction period. The presence of an induction period is also observed in the reduction of a $\sim5\times10^{-2}$ mol litre^{-1} solution of Pu(VI) in 1 M HNO_3 and of a 1×10^{-2} mol litre^{-1} solution of Pu(VI) in 0.3 M HNO_3.

An induction period is a typical feature of autocatalytic processes. Autocatalytic reduction of Pu(VI) was observed for the first time about 40 years ago during α-radiolysis of nitric acid solutions of Pu(VI). It was suggested that slow accumulation of Pu(V) and its disproportionation give rise to Pu(IV). The latter reacts with HNO_2 and H_2O_2 thus yielding Pu(III), which reduces Pu(VI) and Pu(V).

It has been shown [125] that when Pu(IV) is added to the starting solution of Pu(VI), the initial rate of reduction of the latter increases and the induction period is shortened. This is true for solutions in which $[\text{Pu(VI)}] > 5\times10^{-3}$ mol litre^{-1}. The addition of Pu(IV) to a solution in which $[\text{Pu(VI)}] \leqslant 5\times10^{-3}$ mol litre^{-1} does not result in acceleration of the reduction; on the contrary, Pu(IV) is oxidised. During γ-radiolysis in HNO_3 solutions, HNO_2 is accumulated.[125]

When Pu(VI) is reduced by nitrous acid, an equilibrium is established. Pu(VI) is consumed in three processes. Firstly, the Pu(V) formed disproportionates. Secondly, Pu(IV) reacts with Pu(V), and the resulting Pu(III), in its turn, reacts with Pu(VI), *i.e.* the corresponding equilibrium is established. Thirdly, Pu(IV) is reduced with nitrous acid, and Pu(III) reacts with Pu(VI) and Pu(V).

The overall rate of reduction of Pu(VI) and the rate of its reduction by nitrous acid were calculated.[125] The latter was found to be 2–3 times lower than the observed rate. Therefore, it was suggested that Pu(VI) and Pu(IV) are reduced by the precursors of nitrous acid, namely, e_{aq}^- and H. It was also found that the degree of reduction of Pu(VI) depends on its concentration and on the concentration of HNO_3.

The kinetics of reduction of Pu(VI) for various conditions of γ-irradiation have been calculated.[127] The results of calculations were in satisfactory agreement with experimental data. However, it has been noted [128] that for 1 M HNO_3 with $[\text{Pu(VI)}] = 1\times10^{-2}$ mol litre^{-1} and for 3 M HNO_3 with $[\text{Pu(VI)}] = 0.1$ mol litre^{-1}, the reaction of Pu(VI) with hydrogen peroxide should also be taken into account. When deaerated nitric acid solutions of mixtures of Pu(III) and Pu(IV) are exposed to X-rays, Pu(V) and, possibly, Pu(VI) are accumulated. The initial oxidation yield decreases from 0.052 to ~0.004 ion (100 eV)$^{-1}$ as the concentration of HNO_3 increases from 0.3 to 2 M. The introduction of nitrate ions leads to a decrease in the yield of oxidation.

The behaviour of Pu(IV) ions during γ-radiolysis in nitric acid has been studied in detail.[129] In a 0.3 M solution of HNO_3 at $[\text{Pu(IV)}]_0 = 1\times10^{-3}$ mol litre^{-1} [owing to disproportionation of Pu(IV), the solution contained some quantities of Pu(III) and Pu(VI)] and at a dose rate of 2.17 Gy s^{-1}, oxidation of Pu(IV) is observed. When the $[\text{Pu(IV)}]_0$ value is increased to 8×10^{-3} mol litre^{-1}, the oxidation occurs only at the beginning of irradiation, and then reduction of Pu(VI) occurs instead. When the dose rate (I) is equal to 1.33 Gy s^{-1}, reduction of Pu(VI) is also observed. In a 1 M solution of HNO_3 containing 1×10^{-2} mol litre^{-1} of Pu(IV) at $I = 1.33$ Gy s^{-1}, a steady state is established after accumulation of $\sim1\times10^{-3}$ mol litre^{-1} of Pu(VI). The process of oxidation in 6 M HNO_3 at $[\text{Pu(IV)}]_0 = 1\times10^{-2}$ mol litre^{-1} and $I = 2.17$ Gy s^{-1} occurs at a constant rate up to a dose of ~1 MGy. The initial oxidation yields depend on the concentrations of Pu(IV) and HNO_3 and on the dose rate. The concentration of the nitrous acid formed was also measured in the study cited. To estimate the yields of oxidation of Pu(IV), equations were proposed that permit prediction of its behaviour under various conditions.

In a study of γ-radiolysis of solutions of Pu(III) in nitric acid, it has been found that in the case of deaerated solutions, the initial yields of Pu(IV) and HNO_2 are identical and amount to 7.8 ion (100 eV)$^{-1}$.[128] In solutions saturated with oxygen, G[Pu(IV)] = 8.4 ion (100 eV)$^{-1}$, whereas $G[HNO_2]$ is close to zero.

The initial yields of Pu(IV) both in deaerated solutions and in solutions saturated with oxygen are close to the following value:

$$G_{e_{aq}^-} + G_H + G_{OH} + 2G_{H_2O_2} = 8.2 \text{ molecule (100 eV)}^{-1}.$$

Evidently, hydrated electrons and H atoms react in this system with nitrate ions and with non-dissociated nitric acid to give NO_3^{2-} and HNO_3^-, respectively; these species are finally converted into NO_2 and N_2O_4. Nitrogen dioxide and its dimer are able to oxidise Pu(III).[128] The OH radicals participate in the oxidation of Pu(III) and in the reactions with NO_3^- and HNO_3 to give NO_3 radicals. The latter oxidises Pu(III). Hydrogen peroxide, apparently, reacts slowly with Pu(III), each molecule of the peroxide oxidising two Pu(III) ions (*via* the intermediate formation of OH radicals). In solutions saturated with oxygen, H atoms partly react with oxygen thus yielding HO_2 radicals; each of these radicals is able to oxidise

three Pu(III) ions. Therefore, the initial yield of Pu(IV) in these solutions is somewhat higher than that in deaerated solutions.

In conformity with the proposed mechanism, the initial yield of HNO_2 should be equal to $G_{e^-_{aq}} + G_H = 3.65$ ion $(100\ eV)^{-1}$. The value found experimentally [128] for deaerated solutions is markedly higher. However, in solutions saturated with oxygen, the yield of HNO_2 is close to zero.[128] This casts doubt on its high yield in deaerated solutions.

When the radiation doses are high, the quantity of Pu(IV) formed is sufficient for its reaction with nitrous acid. This should result in a decrease in the yield of Pu(IV), and this is actually observed in the experiment.[128]

The influence of U(VI) ions on the radiolytic transformations induced by X-rays of plutonium ions in deaerated 0.3 M solutions of HNO_3 has been studied.[1] The initial oxidation yield of plutonium was found to decrease from 0.05 ion $(100\ eV)^{-1}$ observed in the absence of U(VI) to zero for solutions containing 0.3 mol $litre^{-1}$ of U(VI). At higher concentrations of U(VI), plutonium is reduced. The introduction of dichromate ions in U(VI)-containing solutions of plutonium in nitric acid results in oxidation of plutonium accompanied by reduction of $Cr_2O_7^{2-}$. The dependences of the behaviour of plutonium on the ratio of concentrations of hexavalent chromium and uranium, on the concentration of HNO_3 and on the radiation dose were investigated.

Study of radiolytic transformations of Pu(VI) in 3 M HNO_3 in the presence of U(VI) has demonstrated that the introduction of U(VI) shortens the induction period observed for the reduction of plutonium in the absence of uranium ions.[126] A similar phenomenon was observed in solutions containing Pu(IV) and Pu(VI). It was shown that U(V) resulting from radiolysis reduces Pu(VI) and Pu(IV).

The behaviour of Pu(IV) and Pu(VI) ions in 4 M solutions of HNO_3 exposed to high-energy electron pulses generated by a U-12 linear electron accelerator has been studied.[130] It was found that, irrespective of the ratio of the concentrations of Pu(IV) and Pu(VI), the dose rate (for medium dose rates of 35–200 Gy s^{-1}) and the temperature (in the range 10–90 °C), the irradiation results in the reduction of Pu(VI) to Pu(IV). In some cases, $G[-Pu(VI)]$ is proportional to $I^{-1/2}$; the rate of reduction was found to depend on the temperature. The mechanism of radiolysis of this system has been discussed comprehensively by Tkhorzhnitskii and Egorov,[131] who proposed an equation for the reduction yield of Pu(VI) [or the yield of formation of Pu(IV)]. This equation relates G[Pu(IV)] to I, [Pu(V)] and [Pu(III)]. However, the dependence of the yield of Pu(IV) on I found by these researchers differs from that described in a previous study.[130]

To elucidate the role of polyvalent ions in the reduction of plutonium induced by pulse electron radiation, 4 M solutions of HNO_3 containing Pu(VI), Pu(IV), U(VI), Ru, Rh, Pd, Mo, Ce and other elements have been studied.[130] It was found that Pu(VI) is reduced only when uranium and palladium are present simultaneously. Uranium(VI) increases the 'reducing capacity' over the whole process, whereas Pd(II) is active only at the beginning of the process.[131] On exposure to radiation, U(VI) is converted into U(V), while Pd(II) transforms into Pd(I), Pd(III) and Pd(IV); the latter results from disproportionation of Pd(III). Palladium(IV) is reduced by nitrous acid, U(V), Pd(I), Pu(III), Pu(IV) and Pu(V) to give Pd(II). This accounts for the fact that Pu(IV) is partly oxidised during the radiolysis of its solutions in the presence of Pd(II) but in the absence of U(VI). Note that the reduction yield of Pu(VI) in the presence of U(VI) and Pd(II) decreases with an increase in the radiation dose.

Radiolytic transformations of Pu(VI) in 0.01–0.1 M solution of HNO_3 containing Np(VI) have been studied.[132] It was found that at a [Pu(VI)]/[Np(VI)] ratio of 12.5, both Pu(VI) and Np(VI) are reduced. Plutonium remains in the solution in the hexavalent state at radiation doses below 320 Gy.

The same researchers [132] studied the reduction of Pu(VI) and oxidation of Pu(IV) in 0.5–4 M solutions of HNO_3 at [Pu]/[Np] ratios of 0.005–0.125. When $[HNO_3] = 0.5$ M, neptunium exists as Np(V), whereas in 2–4 M solutions of HNO_3, some Np(VI) can also be found in the system. It was found that in 0.5 M HNO_3, the reduction of Pu(VI) in the presence of neptunium occurs when $[Pu] \geqslant 5 \times 10^{-4}$ mol $litre^{-1}$, the rate of the reduction being higher than that in the absence of neptunium. At the same time, in 2–4 M solutions of HNO_3, reduction of Pu(VI) mixed with neptunium is observed at $[Pu] \geqslant 10^{-2}$ mol $litre^{-1}$. The reduction of Pu(VI) starts after an induction period corresponding to a 75%–80% reduction of Np(VI). The reduction yield depends on the concentration of plutonium and does not depend on the concentration of HNO_3. In the absence of neptunium, the rate of reduction decreases with an increase in the concentration of the acid.

Radiolytic oxidation of Pu(IV) in the presence of neptunium in 0.5 M HNO_3 has been studied.[133] It was found that the smaller the concentration of plutonium, the larger its proportion being oxidised. In the presence of Pu(VI), the rate of oxidation decreases. After prolonged irradiation, steady-state concentrations of Pu(VI) and Pu(IV) are established. The mechanism for the γ-radiolysis of this system was proposed, equations were derived and the concentrations of Pu(VI) at various doses were calculated.[133]

2. α-Radiolysis of acidic aqueous solutions of plutonium ions

In the majority of cases, α-radiolysis of plutonium induced by its own radiation has been studied. Sometimes α-radiolysis results in the oxidation of plutonium; however, most often it leads to a decrease in its average oxidation number.

As early as the 1940–1950s it was found [1] that the rate of reduction of Pu(VI) induced by α-radiation in 0.48–1.9 M solutions of $HClO_4$ containing either only Pu(VI), or Pu(VI) + Pu(IV), or Pu(VI) + Pu(IV) + Pu(V) obeys zero-order kinetics, the rate constant k being equal to 1.18×10^{-2} $days^{-1}$. The reduction yield is expressed by the following equation

$$G[-Pu(VI)] = k(100T_{1/2}/0.693E), \quad (10)$$

where $T_{1/2}$ is the half-life of the corresponding plutonium isotope (days) and E is the average energy of α-particles (eV).

The half-life of ^{239}Pu is 2.411×10^4 years, $E = 5.106$ MeV (11.8%), 5.144 MeV (15%) and 5.157 MeV (73%).[134] It follows from Eqn. (10) that $G[-Pu(VI)] = 2.92$ ion $(100\ eV)^{-1}$.

Under the action of its own α-radiation, Pu(VI) is reduced to Pu(V); the latter disproportionates. The Pu(IV) thus formed reacts with Pu(V) to give Pu(III) and Pu(VI).[1] Reduction of Pu(VI) in 0.2 M $HClO_4$ under the action of α-particles emitted by ^{210}Po has been studied.[123] When the radiation dose is lower than 3 kGy, Pu(V) forms in the solution, and $G[-Pu(VI)] = 3.2$ ion $(100\ eV)^{-1}$. When the dose is higher than 3 kGy, Pu(IV) is formed, and $G[-Pu(VI)] = 1.6$ ion $(100\ eV)^{-1}$. Finally, when the dose exceeds 11 kGy, Pu(III) is accumulated, and $G[-Pu(VI)] = 1.1$ ion $(100\ eV)^{-1}$. These results do not depend on whether or not air is present in the solution. The theoretical yield for the reduction of Pu(VI) to Pu(V) is 3.0 ion $(100\ eV)^{-1}$, which is in agreement with the experimental result.

In a 1 M solution of $HClO_4$ containing ~0.01 mol $litre^{-1}$ of $^{239}Pu(IV)$ (at 25 °C), the average oxidation number of plutonium changes by 0.014 every day until it becomes 3.02–3.05.[1] The gas evolved from the solution consists of oxygen (60%) and hydrogen (40%). The solution was found to contain a substantial amount of chloride ions, which obviously had been formed by the action of ionising radiation on the perchlorate ions. The theoretical reduction yield of Pu(IV), like that for the reduction of Pu(VI), is 3.0 ion $(100\ eV)^{-1}$. The $G[-Pu(IV)]$ value calculated from an equation similar to Eqn. (10) is 3.5 equivalent $(100\ eV)^{-1}$. The slight difference between these values can be due to the fact that Pu(IV) accepts some of the reducing radicals from the spurs.

The radiolytic transformations of $^{238}Pu(IV)$ and $^{238}Pu(VI)$ in 1 M $HClO_4$ have been described.[135] The radiation dose rate was ~0.15 Gy s^{-1}. The concentration of Pu(IV) remained constant, whereas Pu(VI) was reduced to give Pu(IV) and Pu(III). Using the data presented in this study, we calculated that $G[-Pu(VI)] =$ ~0.16 ion $(100\ eV)^{-1}$. The reduction yield is so low, because in the 1 M solution of $HClO_4$, the reaction between Pu(VI) and H_2O_2

occurs slowly; therefore, hydrogen peroxide is accumulated and can react with OH, H and e_{aq}^- in the bulk of the solution and in the spurs.

An increase in the dose rate of α-radiation by 3–4 orders of magnitude somewhat changes the course of radiolysis. Study of the reduction of Pu(VI) in 2 M $HClO_4$ under the action of the α-particles emitted by ^{244}Cm (at a dose rate of 3.95 Gy s^{-1}) has led to the following results.[108] Initially, the concentration of Pu(VI) slowly decreases [we calculated the reduction yield to be 0.01 ion $(100\ eV)^{-1}$], and then, after ~82%–83% of Pu(VI) has been consumed (this takes ~100 h), its concentration starts to increase $\{G[Pu(VI)] = 0.003$ ion $(100\ eV)^{-1}\}$.

When a solution of Pu(VI) in a 0.11 M solution of H_2SO_4 is exposed to α-particles, Pu(IV) is formed;[123] $G[-Pu(VI)] = G[Pu(IV)] = 3$ equivalent $(100\ eV)^{-1}$. The mechanism of reduction is identical to that observed in the case of solutions in perchloric acid. The reduction yield of Pu(VI) barely depends on the concentration of H_2SO_4 as it varies from 0.001 M to 0.3 M and is close to 3 equivalent $(100\ eV)^{-1}$ (see Ref. 1).

It was found[1] that on exposure to α-radiation, Pu(VI) and Pu(IV) ions in 0.06–1.5 M solutions of HCl are reduced at a rate of 1%–0.3% of the average oxidation number per 24 h. Study of the radiolytic reduction of Pu(IV) in a solution of a mixture of $HClO_4$ and HCl has demonstrated that $G[-Pu(IV)]$ diminishes as $[HClO_4]$ decreases and as [HCl] increases. For example, in 1 M $HClO_4$, the yield is 3.5 equivalent $(100\ eV)^{-1}$ whereas in 1 M HCl, it is equal to zero. Plutonium ions in low oxidation states are oxidised in $HClO_4$ solutions containing 0.1 mol $litre^{-1}$ of Br^-. Evidently, this is accomplished *via* the same reactions as the oxidation during α-radiolysis in hydrochloric acid.

Study of the behaviour of $^{238}Pu(OH)_4$ in solutions of NaCl has shown[135–137] that when [NaCl] is less than 3 M, Pu(IV) is oxidised to Pu(V), while at [NaCl] > 3 M, Pu(IV) is converted into Pu(VI). The mechanism of radiolysis includes trapping of OH radicals from the spurs and the formation of oxidising agents (Cl, Cl_2^-, HClO, ClO^-). The yield of H_2O_2 should diminish with an increase in the concentration of NaCl. In solutions containing less than 3 mol $litre^{-1}$ of NaCl, the yield of H_2O_2 [expressed in equivalent $(100\ eV)^{-1}$] is apparently half that of the oxidising agents. The latter convert Pu(IV) into Pu(V) and Pu(VI); the hexavalent plutonium is reduced by hydrogen peroxide to Pu(V), which is stable in the presence of H_2O_2. In solutions containing more than 3 mol $litre^{-1}$ of NaCl, the yield of H_2O_2 is low, and thus Pu(VI) is not reduced and is accumulated or is reduced to a small extent.

Radiolytic transformations of plutonium ions in concentrated solutions of NaCl have been studied.[138] This study was undertaken in view of the intended burial of solid radioactive wastes in depleted salt pits. It was noted that the reaction of PuO_2^{2+} with hypochlorite ions resulting from α-radiolysis of these solutions plays an important role in the process.

In a study of the reduction of Pu(VI) ($\sim 7\times10^{-3}$ mol $litre^{-1}$) in solutions of $NaNO_3$ (the initial pH value was 3), it has been shown that Pu(V) is accumulated initially, and then the process gradually decelerates. At this time, formation of Pu(IV) as a colloid begins. It was found[1] that the $G[-Pu(VI)]$ value changes from 4.4 to 7.2 ion $(100\ eV)^{-1}$ as the concentration of NO_3^- ions increases from 0.1 to 5 mol $litre^{-1}$. An equation for calculating the theoretical $G[-Pu(VI)]$ values in these systems was derived, and the calculated values were compared with experimental results.[1]

The data on the α-radiolysis of solutions of HNO_3 with concentrations of less than 0.5 mol $litre^{-1}$ have been discussed in the monograph cited.[1] It was noted that under these conditions, only H_2O_2 is accumulated. It has been calculated[139] that in a 0.4 mol $litre^{-1}$ solution of ^{239}Pu (at a dose rate of 2.7×10^{-3} Gy s^{-1}), the rate of formation of H_2O_2 is equal to 2×10^{-6} mol $(litre\ h)^{-1}$, and over a period of 30 days the concentration of Pu(VI) should decrease by ~25%. However, this does not occur in reality, because after 30 days, the induction period is completed. The low initial rate of reduction of Pu(VI), present in a concentration of less than 0.01 mol $litre^{-1}$ in HNO_3 solutions, is presumably due to its reverse oxidation by nitrous acid.[139]

The reduction of Pu(VI) in solutions of nitric acid induced by its own α-radiation has been studied by many investigators.[1,139–143] The following characteristic features of this process are noteworthy.

Reduction in solutions with pH 3.8 at $[Pu(VI)] = 8\times10^{-3}$ mol $litre^{-1}$ is characterised by an induction period. In more dilute solutions, Pu(VI) is reduced without an induction period. The initial reduction yields vary from 4 to 6 equivalents $(100\ eV)^{-1}$.[1] In 1–4 M solutions of HNO_3, Pu(VI) is reduced to Pu(IV);[141] in more dilute solutions of nitric acid, Pu(III) is also formed.[1,139] When $[HNO_3]$ is more than 0.5 M, α-radiolysis of solutions of Pu(VI) is accompanied by accumulation of HNO_2. The introduction of Pu(IV) shortens the induction period but has only a slight influence on the maximum rate of reduction of Pu(VI).[1,139]

It has been found[141] that in 4–6 M solutions of HNO_3, plutonium remains in the tetravalent state for several years if the dose rate of α-radiation does not exceed 0.3 Gy s^{-1}. At higher dose rates, Pu(VI) is accumulated. The yield of Pu(VI) depends on the concentration of HNO_3; as it increases from 0.9 to 9 M, the yield decreases from 0.0013 to 0.0008 ion $(100\ eV)^{-1}$. An increase in the dose rate also decreases the yield of Pu(VI). In the opinion of the researchers cited,[141] Pu(IV) is oxidised *via* the reactions with OH radicals and nitrogen oxides; hydrogen peroxide acts as a reducing agent. The decrease in the rate of reduction upon an increase in the concentration of HNO_3 was explained by the formation of a complex of Pu^{4+} with nitrate ions.

The behaviour of Pu(VI) and Pu(IV) in nitric acid solutions exposed to intense α-radiation has been investigated in greater detail in other studies.[1,142,143] In 6 M solutions of HNO_3 containing up to 0.1 mol $litre^{-1}$ of Pu(IV) under a dose rate of 4.6 Gy s^{-1}, Pu(VI) is accumulated; the rate of its formation gradually decreases, and finally a steady state is established. The initial rate of oxidation depends linearly on the concentration of Pu(IV). In solutions containing less than 1.8×10^{-2} mol $litre^{-1}$ of Pu(VI), no reduction occurs over a period of 40 days; at $[Pu(VI)] = 1.8\times10^{-2}$ mol $litre^{-1}$, reduction occurs to only a slight extent.[142] When some Pu(IV) is introduced into solutions of Pu(VI), Pu(VI) is reduced to a noticeable extent but not entirely: steady-state concentrations of Pu(IV) and Pu(VI) are established.[140] According to our estimate, the yields of oxidation of Pu(IV) at $[Pu(IV)]_0 \simeq 2\times10^{-3}$ mol $litre^{-1}$ are 0.019 and 0.022 equivalent $(100\ eV)^{-1}$ for 1 and 6 M HNO_3, respectively.

In a study of the reduction of Pu(VI) in 0.3–6 M HNO_3 exposed to the α-radiation from ^{244}Cm, it has been found that at $[HNO_3] > 1$ M, Pu(VI) is reduced to Pu(IV); this process starts after an induction period.[140] This period becomes shorter following an increase in the dose rate and in the concentration of Pu(VI) and becomes longer upon an increase in the concentration of HNO_3. According to our estimate, the reduction yield of Pu(VI) is 0.08 equivalent $(100\ eV)^{-1}$ and it does not depend on the dose rate in the range of 0.95–9.2 Gy s^{-1}. In a 0.3 M solution of HNO_3, hexavalent plutonium is reduced to Pu(V), steady-state concentrations of Pu(V) and Pu(VI) being established.

It was found[142,143] that, Pu(III) in solutions of nitric acid is oxidised on exposure to α-radiation. Under the action of α-particles emitted by curium ($I = 4.2$ Gy s^{-1}), Pu(III) in 0.12 M HNO_3 is partly oxidised to Pu(IV), which forms a peroxide complex. In addition, small amounts of Pu(VI) are accumulated. The degree of conversion of Pu(III) is 20%, and the initial oxidation yield is 3.8 ion $(100\ eV)^{-1}$. When the concentration of HNO_3 increases, the rate and the degree of conversion of Pu(III) increases, and at $[HNO_3] > 1$ M, trivalent plutonium is completely transformed into the tetravalent state. No peroxide complex is formed in solutions containing more than 0.5 mol $litre^{-1}$ of HNO_3. When $[HNO_3] = 2.9$ M, the oxidation yield reaches 74 ion $(100\ eV)^{-1}$, which indicates that a chain process occurs. The introduction of nitrite ions causes a slight increase in the rate of oxidation. The addition of sulfamic acid, which binds HNO_2, decelerates the oxidation or even completely terminates it.

In our opinion, in a 0.12 M solution of HNO_3, nitrate ions trap almost all the reducing radicals from the spurs. Therefore, OH and HO_2 radicals and nitrous acid act as the main oxidants for plutonium(III), *i.e.*:

$$G[-\mathrm{Pu(III)}] = G_{e^-_{aq}} + G_H + G_{OH} + G_{HO_2} + 2G_{H_2} . \qquad (11)$$

If we substitute the yields of the products of water radiolysis (see Table 2) in Eqn. (11), we obtain an oxidation yield equal to 3.9 ion $(100\ eV)^{-1}$, which coincides with the experimental result.[142, 143]

When the concentration of HNO_3 increases, the yield of oxidants decreases owing to the reaction between HNO_2 and H_2O_2; however, HNO_2 (or NO, according to another reaction scheme) reduces nitric acid and thus a chain process develops leading to high oxidation yields. Sulfamic acid binds not only HNO_2 but, apparently, also the oxidising radicals, namely, OH and NO_3. Therefore, oxidation slows down or even stops.

A series of studies [144–151] have been devoted to the mathematical modelling of processes that occur in solutions of nitric acid containing plutonium ions and exposed to γ- or α-radiation. The influence of various factors on these processes, for example, the concentration of HNO_3, oxidation states of plutonium and radiation dose rate, was considered. The calculations were based on experimental results obtained for about 30 reactions. The modelling made it possible to interpret the course of the process and the contributions of individual stages. In some cases, the rate constants for the reactions were estimated; however, they did not always coincide with the values measured experimentally.

Study of the α-radiolysis of solutions of Pu(VI) and Np(VI) in nitric acid has shown that Pu(VI) is not reduced until all the Np(VI) present has been reduced.[131] To elucidate the mechanism of the process, a set of differential equations based on kinetic regularities were composed and numerical integration with known initial conditions was carried out. Comparison of experimental results demonstrated that the period of 'retention' of Pu(VI) depends on the $[Pu(VI)]_0/[Np(VI)]_0$ ratio. The main feature characterising the radiolysis in the system under consideration is that Np(VI) is reduced more rapidly. The decrease in the rate of reduction of Pu(VI) in the presence of Np(VI) was explained not only by the fact that the latter reacts faster with hydrogen peroxide and with nitrous acid but also by the fact that Np(VI) reacts with Pu(V).

Study of the radiolysis of solutions of nitric acid containing Np(IV) and Pu(IV) induced by the α-radiation of ^{244}Cm has shown that the initial rates of accumulation of Np(V) and consumption of Pu(IV) differ from those for systems containing only Np(IV) or Pu(IV).[152] In particular, it was noted that the rate of oxidation of Np(IV) increases, (among other reasons) due to oxidation of Np(IV) by Pu(IV) ions. A model for the radiolysis in this system was proposed and the redox processes occurring in the system were described using 42 reactions.

3. Gas evolution in the radiolysis of acidic solutions of plutonium ions

During some technological operations involving aqueous solutions of plutonium in nitric acid, the formation of explosive gas mixtures is possible. Primary attention in the study of gas evolution during radiolysis is paid to prevention of the formation of these mixtures. Before 1980, gas evolution during radiolysis had been measured many times. In the case of α-radiolysis, gases are formed in markedly higher yields than upon γ-radiolysis.[1]

α-Radiolysis of solutions of plutonium (0.188–0.42 mol litre^{-1}) in 1–9.9 M HNO_3 has been found to be accompanied by the formation of hydrogen, oxygen, nitrogen, dinitrogen oxide and nitrogen monoxide (hydrogen is the component formed in the highest yield). The yields decrease from 0.2 to 0.018 molecule $(100\ eV)^{-1}$ as the concentration of HNO_3 increases from 1 to 9.9 M. The yields of oxygen for these concentrations are 0.082 and ~0 molecule $(100\ eV)^{-1}$. The yields of nitrogen, dinitrogen oxide and nitrogen monoxide in a 9.7 M solution of HNO_3 are equal to 0.043, 0.0031 and 6×10^{-4} molecule $(100\ eV)^{-1}$, respectively.

Several samples of a 8.5 M solution of HNO_3 containing ~1 mol litre^{-1} of Pu(IV) have been stored for 52 months. Gases were formed in the following average yields, molecule $(100\ eV)^{-1}$: G(the sum of gases) = 0.060, $G(H_2)$ = 0.033, $G(O_2)$ = 0.021, $G(N_2)$ = 0.005; traces of nitrogen oxides were also detected.

The decrease in the concentration of hydrogen upon an increase in the concentration of HNO_3 (and, obviously, plutonium ions) is due to trapping of reducing radicals from the spurs, which suppresses the formation of hydrogen. Molecular oxygen arises upon the direct action of the radiation on NO_3^- and HNO_3 and also upon the reactions of H_2O_2 and HO_2 with plutonium ions [mostly with Pu(IV)]. In 1 M HNO_3, the yield of O_2 resulting from the direct action can be neglected. The $G(O_2)$ value is much smaller than $G_{H_2O_2}$; this is due to the reaction between HNO_2 and H_2O_2. As the concentration of HNO_3 increases, the rate of this reaction increases; therefore, $G(O_2)$ decreases. Nitrogen and its oxides appear upon direct action of the radiation on NO_3^- and HNO_3.

We calculated $G(H_2)$ values for the α-radiolysis of solutions of Pu(IV) (50 g litre^{-1}). For solutions in 1 M HNO_3, 1 M $HClO_4$ and 0.1 M H_2SO_4, the following values were found, molecule $(100\ eV)^{-1}$: 0.21, 0.38 and 1.6, respectively. In our opinion, the fact that the yields attained in HNO_3 and $HClO_4$ are smaller than that in H_2SO_4 can be explained in the following way. In a dilute solution of H_2SO_4, Pu(IV) ions form sulfato-complexes, which react with e^-_{aq} and H more slowly than the aqua-complex. In addition, in solutions of sulfuric acid, Pu(III) is oxidised by the H atoms, and this process affords H_2. In HNO_3 and $HClO_4$ solutions, plutonium ions accept more precursors of H_2 from the spurs than in H_2SO_4.

An equation has been reported,[153] which permits the calculation of the amount of hydrogen evolved from highly radioactive wastes containing, among other components, nitrates and plutonium. The yields of hydrogen evolved by plutonium-containing brines under the action of α-particles emitted by ^{239}Pu vary from 0.6 to 1.5 molecule $(100\ eV)^{-1}$ depending on the composition of the brine.[154] It has been noted [155] that the yield of hydrogen in the α-radiolysis of nitrate-containing solutions of plutonium almost does not depend on the form [Pu(IV) or Pu(VI)] in which plutonium occurs in the system.

4. Radiolysis of alkaline aqueous solutions of plutonium

During γ-radiolysis of aerated alkaline solutions of Pu(VI), plutonium is first reduced to Pu(V) and then to Pu(IV).[63, 156] The reduction yield is 1.5–1.6 ion $(100\ eV)^{-1}$, irrespective of the concentration of alkali, over the concentration range studied (1 to 6 M). As in the case of γ-radiolysis of alkaline aqueous solutions of Np(VI), specific 'oscillations' in the variation of the optical density of the solution exposed to radiation are observed. The oscillations include an initial decrease in the intensity of absorption of Pu(VI) caused by its reduction to Pu(V), its subsequent increase caused by the formation of a fine suspension and light scattering from its particles, a further decrease in the absorption intensity caused by precipitation, *etc*. However, as distinguished from γ-radiolysis of alkaline solutions of Np(VI), in this case, no peroxide complex of Pu(V) was detected in nitrate-containing solutions; this is due to the low stability of this complex.

The mechanism of radiolytic transformations of Pu(VI) in aerated alkaline solutions is similar to that for Np(VI). The main distinction is that the Pu(V) resulting from reduction disproportionates to give Pu(IV) and Pu(VI).[63, 156]

Radiolysis of alkaline aqueous solutions of Pu(VI) in the presence of acceptors of radical reducing agents transforming them into radicals acting as oxidants affords Pu(VII) ions. This was observed for the first time by Pikaev *et al.*[118] In this study, alkaline solutions of Pu(VI) saturated with dinitrogen oxide were exposed to radiation. As noted above, dinitrogen oxide reacts with e^-_{aq} yielding the O^- radical anion. More recently, oxidation of Pu(VI) has been studied more comprehensively.[157] With allowance for the induction effect, the initial yield of Pu(VII) in a 1 M solution of NaOH was equal to 5.4 ion $(100\ eV)^{-1}$. The mechanism of radio-

lytic oxidation of Pu(VI) in alkaline solutions is similar to that for Np(VI).

The formation of Pu(VII) has also been observed [158, 159] in the γ-radiolysis of aerated solutions of Pu(VI) in 1 M NaOH in the presence of $S_2O_8^{2-}$. It was found that G[Pu(VII)] = 4.0 ion (100 eV)$^{-1}$ at [Pu(VI)] = 5.1×10^{-4} and [$S_2O_8^{2-}$] = 0.07 mol litre^{-1}. This value is close to the yield of Np(VII) obtained in a 1 M solution of NaOH containing $S_2O_8^{2-}$ ions. These ions react with e_{aq}^-, and the $S_2O_8^{3-}$ ion radicals thus formed react with OH^- and are finally converted into O^-. The experimental G[Pu(VII)] value is lower than the calculated value [$\sim$4.7 ion (100 eV)$^{-1}$]; this is apparently due to the occurrence of side reactions of O_3^- ion radicals (resulting from the reaction of O^- with O_2) and/or $S_2O_8^{3-}$ ion radicals. When [Pu(VI)] = 5×10^{-3} mol litre^{-1}, the yield of Pu(VII) amounts to $\sim$2 ion (100 eV)$^{-1}$. The decrease in the yield compared to that attained in more dilute solutions of Pu(VI) is due to the fact that in an alkaline medium the stability of the $S_2O_8^{3-}$ ion radicals can be relatively high and sufficient for them to react partly with Pu(VI).

The irradiation of aerated alkaline solutions of Pu(VII) results in its reduction.[157] The reduction yield does not depend on the concentrations of Pu(VII) (the concentration range used was $2.4 \times 10^{-4} - 1 \times 10^{-3}$ mol litre^{-1}) or the alkali (in the range 0.87 – 3.5 M); it is 2.35 ion (100 eV)$^{-1}$. The mechanism of the process has been discussed previously.[1]

The behaviour of Pu(IV) and Pu(VI) in 1 – 15 M solutions of NaOH containing nitrate ions has been studied.[160] The solutions were irradiated for 2 years by α-particles emitted by plutonium. Initially, Pu(V) was accumulated in the solution over the precipitate of Pu(IV) hydroxide and then its amount decreased. The decrease in the concentration of Pu(V) began after 1 – 2, 7, 20 and 56 days in 1, 2 – 9, 10 and 15 M solutions of NaOH, respectively.

The researcher cited [160] did not discuss what oxidising and reducing agents could have been involved in the reactions in this system. He attributed the decrease in the concentration of Pu(V) to a change in the degree of crystallinity of Pu(IV) hydroxide. In our opinion, two processes occur in this system, namely, oxidation of Pu(IV) in the precipitate and reduction of Pu(V) in the bulk of the solution. The oxidation is accomplished by O^- radical ions and hydroperoxide HO_2^-. Note that HO_2^- is able to oxidise freshly precipitated Pu(IV) hydroxide.[161] The reduction of Pu(V) might be accomplished by e_{aq}^-, H and NO_3^{2-} ion radicals (resulting from reactions of e_{aq}^- and H with nitrate ions). According to our estimates, G[−Pu(V)] decreases from 15.5 to 2.6 ion (100 eV)$^{-1}$ as the concentration of NaOH increases from 1 to 15 M. These high yields may be associated not only with Pu(V) ions but also with plutonium in a colloidal form.

Hexavalent plutonium introduced in alkaline solutions is gradually reduced.[161] The initial reduction yields, which we have determined using the data about the variation of the concentration of Pu(VI) reported by Delegard,[160] decrease from 25.2 to 2.6 ion (100 eV)$^{-1}$ as the activity of NaOH increased from 0.6 to 3.4 M. If we assume that the yields of the products of the α-radiolysis of water in alkaline solutions are equal to those in sulfuric or perchloric acid, the theoretical reduction yield of Pu(VI) to Pu(V) should be $\sim$3 ion (100 eV)$^{-1}$. The higher values could be due to the presence of organic impurities and/or co-precipitation of Pu(VI) with Pu(V). As time goes on, some Pu(V) in the precipitate is converted into Pu(IV); therefore, the colour of the precipitate changes.[160]

VII. Americium

1. γ-Radiolysis of aqueous solutions of americium ions

The studies performed before 1980 dealt with γ-radiolysis of weakly acidic solutions of Am(III) saturated with dinitrogen oxide and solutions of Am(VI) in nitric or in phosphoric acid and alkaline solutions of Am(VI). The most significant results are presented in Table 18.

The method of pulse radiolysis with fast recording of short-lived species has been used to elucidate the mechanism of radiolytic oxidation of Am(III).[52, 165] It was found that short-lived Am(IV) ions are formed intermediately in this process; these ions were identified based on the broad optical absorption band with a maximum at 340 nm, which appears under the action of an electron pulse. Based on the accumulation of Am(IV), the rate constants for the reaction of Am(III) with OH under various conditions were measured (see Table 6). This reaction has also been studied by pulse radiolysis (see, for example, Refs 30 and 166).

In solutions of Am(III) saturated with N_2O, Am(IV) ions are consumed in a second-order reaction. For [Am(III)]$_0$ > 2×10^{-3} mol litre^{-1}, this reaction was found to be disproportionation of Am(IV). The rate constants for this process ($2k$ values) at pH 2.0 and pH 2.6 – 3.2 are 4.5×10^6 and 6×10^6 litre mol^{-1} s^{-1}, respectively.[52] According to another study,[30] at pH 5.2, the $2k$ value is 1.0×10^7 litre mol^{-1} s^{-1}. When the concentration of

Table 18. Yields of products in the radiolytic transformations of americium in aqueous solutions.[1]

Americium	Radiation	Medium I	Medium II	G /ion(100 eV)$^{-1}$
Oxidation to Am(V)				
Am(III)	γ	$HClO_4$, saturation with N_2O	($\sim$4.0)	0.85
	α	K_2CO_3	3.0 – 5.5	–
	α	NaCl	5.0 (8.3)	0.6 [a]
Reduction to Am(III)				
Am(IV)	α	H_3PO_4	10	–
Am(IV),[b]	α	$HClO_4$	(2.0 – 4.0)	4.4
	α	HNO_3	0.4	8.8
Am(IV)	α	NH_4F	13.0	$\sim$4.0
Am(V)	α	$HClO_4$	0.1 – 2.0	1.2 – 2.3
	α	H_2SO_4	1.0	1.4
	α	HNO_3	0.5 – 9.0	0.019 – 0.61 [c]
	α	HCl	0.5	1.74
	α	$HClO_4 + H_3PO_4$	0.1 + 0.01	1.7
Reduction to Am(V)				
Am(VI)	α	HNO_3	0.1 – 4.7	3.0 – 4.0
	α	HNO_3	See [d]	3.3 – 64.0
	α	$HClO_4$	0.2 – 6.0	3.0 – 4.0
	α	$HClO_4$	12.0	0
	α	H_2SO_4	0.1 – 10.0	1.2 – 4.0
Reduction to Am(III)				
	γ	H_3PO_4	3.0	2.2
	α	H_3PO_4	3.0 and	1.0 – 2.3
			10.0 – 11	1.2 – 4.0
Reduction to Am(V)				
Am(VI)	α	$NaHCO_3$ or K_2CO_3	–	4.0
Reduction to Am(IV)				
Am(VI),[b]	α	$K_{10}P_2W_{17}O_{61}$	$(3.0 – 8.0) \times 10^{-3}$	0.35 [e]
Oxidation to Am(VII)				
Am(VI)	γ	NaOH, in the presence of N_2O or $S_2O_8^{2-}$	1.0 – 3.0	–

[a] The yield was estimated from the data of Ref. 162. [b] Complex with $P_2W_{17}O_{61}^{10-}$. [c] The yields were estimated from the data of Ref. 163. [d] The medium changed from a solution with pH 3.1 to a 14.3 mol litre^{-1} solution of HNO_3. [e] The yields were estimated from the data of Ref. 164.

Am(III) is lower, in addition to the disproportionation of Am(IV), its reactions with HO_2 and H_2O_2 occur in the system.

In aerated solutions, Am(IV) also disappears through a second-order reaction. This is the interaction of Am(III) with HO_2. The rate constants measured for this process are listed in Table 14. It can be seen that the rate constant depends on the pH of the solution. This was explained by the fact that Am(IV) ions are hydrolysed to different extents at different pH values.

The rate constant for the reaction of Am(IV) with hydrogen peroxide was measured (see Table 9). An attempt has been made [52] to determine the rate constant for the reaction between Am(IV) and Am(V). According to an approximate estimate, the upper limit for this rate constant is 3×10^4 litre mol^{-1} s^{-1}.

Pulse radiolysis experiments [30, 31, 166] indicate that the reaction of e_{aq}^- with Am(III) affords Am(II). It is responsible for an absorption band with a maximum at 310 nm [31] or 312 nm.[30] The rate constants found for this reaction are listed in Table 3. The intensity of the optical absorption of this ion decreases with a decrease in the pH of the solution. The Am(II) ion is unstable. At pH 4.7, it disappears with a half-life of 70 μs.[31] When the concentration of Am(III) is large and the dose per pulse is low, Am(II) reacts with water.[30] The rate constant for this reaction is 9.7×10^4 s^{-1}.

The results obtained using pulse radiolysis made it possible to propose a mechanism for the oxidation of Am(III) in the γ-radiolysis of its weakly acidic solutions saturated with N_2O. This mechanism has been discussed in detail previously.[1]

The transformations of Am(VI) ions during the γ-radiolysis have been studied in aqueous solutions containing nitric or phosphoric acid and also in alkaline solutions. In the latter case, irradiation was used to obtain Am(VII).

Based on the possible mechanism of the radiolytic transformations of Am(VI) in nitric acid solutions exposed to γ-radiation, an equation for $G[-\text{Am(VI)}]$ has been derived.[1] Calculations in terms of this equation led to yields of 5.0 and 5.3 ion (100 eV)$^{-1}$ for 0.1 and 1 M solutions of HNO_3, respectively. This is close to experimental results. For a 4.7 M solution of HNO_3, this equation cannot be used, because in this case, the direct action of the ionising radiation on HNO_3 and NO_3^- should be taken into account.

In the radiolysis of solutions of Am(VI) in phosphoric acid, the H_2PO_4 radical, which is an oxidant, plays an important role.[167] Therefore, it cannot be ruled out that this radical, like OH radical, can oxidise the Am(V), Am(IV) and Am(III) ions formed. However, these oxidation reactions might be slow, and recombination of $H_2PO_4^{\bullet}$ to give $H_4P_2O_8$ can compete with them. This provided grounds for the conclusion that the theoretical yield should lie in the range $0.77 \leqslant G[-\text{Am(VI)}] \leqslant 1.4$ ion (100 eV)$^{-1}$. The experimental value is much higher. The possible reasons for this discrepancy have been discussed in the previous monograph.[1]

Under certain conditions, γ-radiolysis of alkaline solutions of Am(VI), like that for neptunium and plutonium, yields Am(VII). Dinitrogen oxide and $S_2O_8^{2-}$ have been used as scavengers for hydrated electrons (see Table 18).[168] The details of the procedure for preparing Am(VII) as well as the mechanism of the oxidation have been considered in the monograph.[1]

2. α-Radiolysis of aqueous solutions of americium ions

Radiolysis of aqueous solutions of americium induced by its own α-radiation has been studied in various media: in nitric, sulfuric, hydrochloric and phosphoric acids, in carbonate-containing solutions, in the presence of sodium bromate, in 'unsaturated' phosphorotungstic acids, *etc*. Radiolytic transformations of Am(VI), Am(V) and Am(III) ions in solutions of perchloric acid have also been studied. With allowance for the possible mechanism of the reduction of Am(VI) in perchloric acid, one can calculate its theoretical yield; it is equal to 3.0 ion (100 eV)$^{-1}$. This result is in agreement only with some of the values found experimentally (see Table 18). The scatter of experimental values for the yields is caused by the use of solutions of different degrees of purity. The reduction of Am(VI) with water contributes somewhat to the process.[169] The decrease in $G[-\text{Am(VI)}]$ to 0 in 12 M $HClO_4$ can be explained by the change in the yields of the products of water radiolysis and by the sharp retardation of the reaction between Am(VI) and H_2O_2.

As Am(V) accumulates in the solution, its reduction by the HO_2 radical or e_{aq}^- becomes possible. Hydrogen peroxide does not react with Am(V) until Am(VI) is fully consumed.

The data on the radiolytic behaviour of Am(VI) presented in Table 18 have been obtained at a dose rate of α-radiation lower than 0.2 Gy s^{-1}. α-Radiolysis of solutions of Am(VI) in 0.1 – 11 M $HClO_4$ at a dose rate of 0.01 – 4.6 Gy s^{-1} has been studied.[170] In this study, ^{244}Cm was used as the source of α-radiation. The initial reduction yield in a 0.13 M solution of $HClO_4$ (I = 2.9 Gy s^{-1}) is 3.1 ion (100 eV)$^{-1}$. When the concentration of the acid is increased to 0.5 – 1 M, the yield decreases somewhat, but when the concentration becomes larger than 2 M, the yield of reduction increases: in a 7 M solution of $HClO_4$, it is ~48 ion (100 eV)$^{-1}$. Obviously, such a high yield is due to the presence of organic impurities.

In the case of 0.2 M solutions of $HClO_4$ containing variable amounts of $NaClO_4$, the yield increases monotonically with an increase in the concentration of $NaClO_4$ and reaches 5.5 ion (100 eV)$^{-1}$ at $[NaClO_4]$ = 7 mol litre^{-1}.[170] The reduction yield was found to depend somewhat on the concentration of Am(VI). When the concentration of $HClO_4$ is 1 M, the yield does not depend on the dose rate; however, in a 5.5 M solution of $HClO_4$, it is proportional to I^2.

It is noteworthy that the increase in the reduction yield at high concentrations of $HClO_4$ or $NaClO_4$, among other reasons, is due to the fact that Am(VI) reacts with the products of radiolytic decomposition of the perchlorate ion. In particular, it has been found [171] that Am(VI) ions are reduced at a relatively high rate when ClO_2 is passed through a solution of Am(VI) in perchloric acid.

In a study of Kornilov *et al*., [171] $G[-\text{Am(VI)}]$ was shown to be independent of the concentration of Am(VI), which is at variance with an earlier study.[170] In fact, in 0.5 M $HClO_4$, the yield is equal to 2.3 – 2.5 ion (100 eV)$^{-1}$ in the range of Am(VI) concentrations of $(1.5 – 6) \times 10^{-3}$ mol litre^{-1}.

During the α-radiolysis in perchloric acid solutions, Am(V) is reduced to Am(III) (see Table 18). An equation for $G[-\text{Am(V)}]$, which is equal to $G[\text{Am(III)}]$, has been obtained [1] with allowance for the mechanism of radiolysis of Am(V) in perchloric acid. Using this equation, it was found that the theoretical yield amounts to 1.5 ion (100 eV)$^{-1}$. Experimental values are close to this result. The fact that the yield increases somewhat at high concentrations of Am(V) ions is due to the fact that these ions trap the reducing radicals from the spurs.

It has been found [172] that prolonged storage of weakly acidic saturated solutions of $NaClO_4$ containing Am(III) and Cm(III) results in the formation of precipitates. The quantity of the precipitate increases with time, and the colour changes from light brown to black. The time required for the formation of the precipitates decreases with an increase in the dose rate. The optical absorption spectrum of the solution above the precipitate exhibits bands typical of Am(V) (4%) and of the products of radiolytic decomposition of ClO_4^- ions. The solution changes from weakly acidic to neutral. X-ray diffraction analysis has shown that the precipitates contain NaCl (80%), $NaClO_3$ (20%) and americium and curium hydroxides. The precipitates were dissolved, and it was found that ~30% of americium in them occurred in the pentavalent state.

Several researchers have studied α-radiolysis of solutions of Am(VI) in sulfuric acid. The values found for the reduction yields of ^{241}Am(VI) vary from 1.2 to 4.0 ion (100 eV)$^{-1}$ (see Table 18). Probably, the processes occurring in the α-radiolysis of solutions of Am(VI) in sulfuric acid and in perchloric acid are the same. In this case, the theoretical $G[-\text{Am(VI)}]$ value should be 3.0 ion (100 eV)$^{-1}$. The differences between the experimental

and calculated values are apparently caused by the same reasons as in the case of solutions in perchloric acid.

It should be noted that the $G[-\mathrm{Am(VI)}]$ values obtained for concentrated solutions of sulfuric acid are smaller than those for dilute solutions. This can be explained by the fact that HSO_4^- ions and sulfuric acid partially trap the OH radicals from the spurs and, hence, the $G_{H_2O_2}$ value decreases. The HSO_4 (or SO_4^-) radicals are oxidants and they, like OH radicals, can oxidise the Am(V) formed.

Pentavalent americium is reduced in solutions of sulfuric acid under the influence of α-radiation (see Table 18). In a solution containing 1 mol litre^{-1} of H_2SO_4, Am(V) is first consumed at a constant rate, and then the rate decreases.

In the case of solutions in nitric acid, the reduction of Am(VI) and Am(V) as well as the influence of $S_2O_8^{2-}$ and BrO_3^- ions on the stability of Am(VI) towards α-radiolysis have been studied. The reduction of Am(VI) during the α-radiolysis in nitric acid includes the same reactions as that during γ-radiolysis. With allowance for this fact, an equation for $G[-\mathrm{Am(VI)}]$ has been derived.[1] Application of this equation to a 0.5 M solution of HNO_3 leads to a theoretical yield of 4.74 ion (100 eV)$^{-1}$. The experimental $G[-\mathrm{Am(VI)}]$ values found by various researchers differ fairly markedly from one another (see Table 18). Apparently, this is due to insufficient purity of the solutions used in some of the studies.

Study of the behaviour of Am(VI) in solutions of HNO_3 and $LiNO_3$ under the action of the α-radiation of ^{244}Cm has shown [173] that at $[HNO_3] \leqslant 6$ M, Am(VI) is reduced to Am(V) [up to the instant when Am(VI) disappears, not more than 4% of Am(III) is accumulated]. At $[HNO_3] > 6$ M, the amount of the Am(III) formed increases. This is due to disproportionation of Am(V). The reduction yields of Am(VI) markedly increase in the presence of $LiNO_3$. According to our estimates, in a 2.9×10^{-3} M solution of Am(VI) containing 0.01 mol litre^{-1} of HNO_3 and 1 mol litre^{-1} of $LiNO_3$, the yield is equal to 48 ion (100 eV)$^{-1}$. If $[LiNO_3] = 9.1$ M, $G[-\mathrm{Am(VI)}] = 75.5$ ion (100 eV)$^{-1}$. In all probability, the so high yields are due to the presence of nonidentified impurities in the solution.

In solutions containing nitric acid, Am(V) is reduced under the influence of α-particles to Am(III) (see Table 18). The reduction yield of Am in 0.01 M HNO_3 almost does not differ from those obtained in dilute $HClO_4$ or H_2SO_4. When $[HNO_3]$ is increased to 4.5 M or $[LiNO_3]$ is increased to 1 M, the interaction of nitrate ions with reducing radicals starts to contribute to the process; therefore, the reduction yield of Am(V) decreases. In 6–9 M HNO_3, disproportionation of Am(V) becomes significant; hence, the observed reduction yield increases.

Study of α-radiolysis of solutions of Am(VI) in nitric acid containing $S_2O_8^{2-}$ ions has shown that at a constant concentration of HNO_3, the reduction yield of Am(VI) decreases upon an increase in the concentration of $S_2O_8^{2-}$. Conversely, when the concentration of $S_2O_8^{2-}$ is constant, $G[-\mathrm{Am(VI)}]$ increases with an increase in the concentration of HNO_3. A detailed interpretation of these findings has been reported previously.[1]

As in the case of Am(VI), $S_2O_8^{2-}$ ions have an influence on the stability of Am(V) ions during the α-radiolysis in solutions of nitric acid. The reduction yields of Am(V) obey complex dependences on the concentrations of Am(V), HNO_3 and $S_2O_8^{2-}$ and on the dose rate. The introduction of bromate ions into a nitric acid solution of Am(V) decreases the rate of its reduction during α-radiolysis.

Pentavalent americium is reduced during the α-radiolysis in hydrochloric acid (see Table 18). The reduction occurs *via* reactions with HO_2, H_2O_2 and with hydrogen atoms resulting from the radiolysis of water and interaction with e_{aq}^-. Chloride ions react with OH radicals in the bulk of the solution and partly in the spurs (in the latter case, this reaction decreases $G_{H_2O_2}$). The Cl_2^- radical ions arising from the interaction of OH with Cl^- can both oxidise Am(V) and react with H_2O_2 (in the latter case, OH is formed). The resulting Am(VI) is reduced by hydrogen peroxide and by chloride ions.

The behaviour of Am(III) in concentrated solutions of NaCl under the action of α-radiation has been studied.[136, 162] Radiolytic transformations of Am(III) in a 5 M solution of NaCl at pH 8.3 was investigated.[162] Americium(V) is formed as the final product of α-radiolysis. The mechanism of radiolysis includes the interaction of OH with Cl^- (formation of Cl_2^-) and, in the opinion of the researcher,[162] the formation of HClO. The ion ClO^- and, perhaps, Cl_2^- act as oxidising agents. The reactions of Cl_2^- with Am(V) and H_2O_2 as well as reactions of Am(VI) with H_2O_2 and Cl^- can occur in this system.

In phosphoric acid, reduction of Am(VI), Am(V) and Am(IV) has been studied (see Table 18). We shall consider the most significant results of these studies. As in the case of γ-radiolysis, Am(VI) is reduced to Am(III); $G[-\mathrm{Am(VI)}]$ is almost independent of the concentration of H_3PO_4 but decreases following an increase in the dose rate. The mechanism of reduction of Am(VI) during the α-radiolysis includes the same reactions as that during γ-radiolysis. As in the case of γ-radiolysis, the yields found experimentally are markedly higher than the calculated values; the possible reasons for this are also the same.

Some studies have dealt with the stability of the complex of Am(IV) with phosphotungstate (see Table 18). The stability of the complex of Am(IV) with $P_2W_{17}O_{61}^{10-}$ depends on the pH and on the concentration of the phosphotungstate ion. Erin *et al.*[164] believe that Am(IV) is reduced both radiolytically and by water. Study of the stability of Am(VI) in solutions of $P_2W_{17}O_{61}^{10-}$ has shown [174] that Am(VI) is converted into Am(IV). According to our estimates, the $G[-\mathrm{Am(VI)}]$ values vary from 3.3 to 0.35 ion (100 eV)$^{-1}$ as the pH changes from 0 to 6.

VIII. Other actinides

Data on the radiolysis of aqueous solutions of transamericium elements are scarce. This is due to the fact that these elements are relatively unavailable and are characterised by short half-lives. Some information about the radiolysis of solutions containing curium, berkelium and californium ions have been reported.

1. Solutions of curium ions

Several studies have been devoted to α-radiolysis of aqueous solutions of Cm(IV) in the presence of complex-forming agents. It has been found [1] that in a 15 M solution of CsF at 10.5 °C, ^{244}Cm(IV) is reduced under the action of its own α-radiation to Cm(III), the rate constant for reduction and the $G[-\mathrm{Cm(IV)}]$ value being equal to 2.17×10^{-4} s^{-1} and 3.08 ion (100 eV)$^{-1}$, respectively. The reduction yield of Cm(IV) should be determined by its reactions with H, e_{aq}^-, HO_2 and H_2O_2 and by the reverse oxidation of the resulting Cm(III) by the OH radical. Unfortunately, since there are no data on the yields of the primary products of α-radiolysis of concentrated aqueous solutions of fluoride ions, it is impossible to calculate the theoretical reduction yield of Cm(IV) and to compare it with the experimental value.

The stability of Cm(IV) prepared by oxidation of Cm(III) on heating with peroxodisulfate in the presence of $K_{10}P_2W_{17}O_{61}$ has been studied.[1, 175] At room temperature (without removal of the oxidant), Cm(IV) is reduced to Cm(III); the yield is 2.63 ion (100 eV)$^{-1}$.

In the presence of the oxidant, the rate of the process in the initial period [before the Cm(IV) is reduced by ~50%] is constant; then a deviation from the linear dependence is observed. For the initial period, $G[-\mathrm{Cm(IV)}]$ is 4.74 ion (100 eV)$^{-1}$. In another study, a complex of Cm(IV) with phosphotungstate has been used.[175] It was found that the consumption of Cm(IV) as well as that of Am(IV) or Cf(IV) obeys the equation

$$-\frac{\mathrm{d[An(IV)]}}{\mathrm{d}t} = k_0 + k_1[\mathrm{An(IV)}], \qquad (12)$$

where k_0 is the rate of the radiation-chemical process.

The reduction yield estimated from the k_0 value is more than 20 ion (100 eV)$^{-1}$ (in the pH range of 1.5–6.1 and at a concentration of the heteropolyanion of 0–0.012 mol litre^{-1}). In the studies under consideration, the concentration of phosphotung-

state exceeded the concentration of curium; therefore, e^-_{aq} and H should react mostly with the heteropolyanion to give 'heteropoly-blue'. The rate constant for the corresponding reaction of e^-_{aq} is $\sim 1.2 \times 10^{11}$ litre mol^{-1} s^{-1}.[5] Therefore, it cannot be ruled out that heteropolyanions accept the precursors of H_2 from the spurs. Evidently, the heteropoly-blue reacts with Cm(IV). The reduction yield can be found from the equation

$$G[-\mathrm{Cm(IV)}] = G_{e^-_{aq}} + G_H + G_{HO_2} + 2G_{H_2O_2} + 2AG_{H_2} - G_{OH}\,, \quad (13)$$

where A is the factor characterising the decrease in the yield of hydrogen caused by trapping of its precursors by heteropoly-anions in the spurs.

In the limiting case, the reduction yield of Cm(IV) in α-radiolysis can reach 5.8 ion (100 eV)$^{-1}$. The high yields reported by Kuno *et al.*[155] are most likely caused by the presence of organic impurities.

Deaerated solutions of Cm(III) containing perchlorate ions and *tert*-butyl alcohol (added as an acceptor of the OH radicals) have been studied by pulse radiolysis.[166] It was found that upon the passage of an electron pulse, an optical absorption with a maximum at 240 nm appears. This absorption was attributed to Cm(III) arising in the reaction with e^-_{aq}. However, the large negative redox potential of the Cm(III)/Cm(II) pair casts doubt upon this interpretation. In a solution saturated with N_2O, the action of an electron pulse gives rise to optical absorption with a maximum at 260 nm. This was assigned to Cm(IV) resulting from the reaction of Cm(III) with OH radicals.

2. Solutions of berkelium ions

Oxidation of Bk(III) induced by γ-radiolysis has been studied in a biphase system consisting of a 6 M aqueous solution of HNO_3 and a 0.2 mol litre^{-1} solution of di(2-ethylhexyl) phosphate (DEHP) in decane.[176] It was found that upon irradiation, berkelium is converted almost entirely into the tetravalent state and is extracted into the organic phase. In this system, Bk(III) is oxidised by NO_3 radicals. The resulting Bk(IV) is partially reduced by nitrous acid and is partially extracted into the organic phase.

In a solution containing 2 mol litre^{-1} of K_2CO_3, trivalent berkelium is oxidised to Bk(IV) under the influence of its own β-radiation. The half-transformation period is 2.5 h, which corresponds to $G[-\mathrm{Bk(III)}] = 5.45$ ion (100 eV)$^{-1}$. The mechanism of the process has been considered in the monograph.[1] Based on this mechanism, an equation for G[Bk(IV)] was obtained; the theoretical yield found from this equation is 8.2 ion (100 eV)$^{-1}$. The experimental result is markedly smaller. It is most likely that, owing to the low concentration of Bk(III), the radicals acting as oxidants are not completely consumed in the reactions with Bk(III) and participate in side processes (for example, they react with H_2O_2 and/or O_2^-).

By virtue of pulse radiolysis, the formation of Bk(II) has been observed upon exposure of a deaerated 2.5×10^{-3} mol litre^{-1} solution of Bk(III) containing *tert*-butyl alcohol (pH 5) to an electron pulse.[32] The appearance of Bk(II) is due to the reaction of Bk(III) with e^-_{aq} (the rate constant for this reaction is presented in Table 3). The absorption spectrum of Bk(II) has a maximum at 310 nm (the molar extinction coefficient at this wavelength is 230 m^2 mol^{-1}). This ion is short-lived; the rate constant for its disappearance is 1.53×10^5 s^{-1}.

The resistance of ^{249}Bk(IV) to its own β-radiation in acidic solutions has been considered in a number of studies (see, for example, Refs 1 and 177–179). In solutions of sulfuric acid, Bk(IV) has been found to be reduced under the influence of its own β-radiation and by water; the $G[-\mathrm{Bk(IV)}]$ values range from 0.83 to 6.5 ion (100 eV)$^{-1}$ and decrease with an increase in the concentration of the acid. In perchloric acid solutions, the reduction yields measured by various researchers vary from 2.4 to 10.2 ion (100 eV)$^{-1}$. The yields of Bk(IV) for several types of solution are listed in Table 19.

The theoretical $G[-\mathrm{Bk(IV)}]$ value can be found based on the mechanism including the reactions of Bk(IV) with H, e^-_{aq}, HO_2 and H_2O_2 and the reaction of the resulting Bk(III) with OH. The presence of air in the solution exerts no influence on $G[-\mathrm{Bk(IV)}]$, because the HO_2 radical resulting from the reaction of H with O_2, like the H atom itself, reduces one Bk(IV) ion. Taking into account the whole set of reactions, we obtain a $G[-\mathrm{Bk(IV)}]$ value of 2.3 ion (100 eV)$^{-1}$. Experimental values are markedly higher in most cases. Evidently, this is due to the presence of organic impurities in the solutions used. The OH radical reacts with RH_2 present as an impurity. The $^{\bullet}RH$ radical thus formed is capable of reducing Bk(IV).

Table 19. The yields of reduction of Bk(IV) in β-radiolysis in various media.

10^3 [Bk(IV)] /mol litre^{-1}	Medium		$G[-\mathrm{Bk(IV)}]$ /ion (100 eV)$^{-1}$	Ref.
	I	II		
6.9–12.7	$HClO_4$	1.0	2.4	177
4.5	$HClO_4$	2.0	2.8	177
3.0	$HClO_4$	3.0	2.9	177
2.6	$HClO_4$	5.0	3.1	177
4.0	HNO_3	0.5	4.3	177
2.4	HNO_3	1.0	4.6	177
3.3	HNO_3	3.0	5.7	177
2.8	HNO_3	6.0	5.9	177
6.7×10^{-2}	HNO_3	9.0	4.7	178
7.0×10^{-2}	HNO_3	9.0	3.6	178
< 0.1	HNO_3 + $AgNO_3$ + $(NH_4)_2S_2O_8$	4.0 + 0.01 + 0.1	0.043	179

Apparently, the most reliable data have been obtained by Erin *et al.*[177] The authors took into account the experience of the earlier researchers and paid primary attention to the purification of the initial sample of ^{249}Bk. It was shown that consumption of Bk(IV) in solutions containing perchloric or nitric acid obeys zero-order kinetics, *i.e.* Bk(IV) is reduced only *via* reactions with the products of water radiolysis. In 2–5 M $HClO_4$, reduction is accomplished by e^-_{aq}, H, H_2O_2, HO_2 and by the products of decomposition of ClO_4^- induced by the direct action of ionising radiation. As a result, the reduction yield is somewhat higher than that in 1 M $HClO_4$. In nitric acid [as in solutions of Am(VI) with similar compositions], H_2O_2 and HNO_2 act as the reducing agents; some of the Bk(III) thus formed is oxidised again by NO_3 radicals.

The relatively high reduction yields of Bk(IV) in sulfuric acid are obviously caused by the presence of organic impurities. The decrease in $G[-\mathrm{Bk(IV)}]$ following an increase in the concentration can be due to the interaction of HSO_4^- with OH radicals, which suppresses the reactions of these radicals with RH_2. The HSO_4 (SO_4^-) radicals are able to oxidise Bk(III); however, they react with organic compounds much more slowly than OH radicals. In addition, in concentrated solutions of H_2SO_4, the HSO_4^- ions partly accept the OH radicals from the spurs, which results in an increase in G_{OH} and a decrease in $G_{H_2O_2}$.

β-Radiolysis of solutions of Bk(IV) in mixtures of perchloric and nitric acids and of perchloric acid with lithium nitrate has been studied.[180] As the content of nitrate ions in the solutions increases, $G[-\mathrm{Bk(IV)}]$ increases as has also been observed for solutions in nitric acid containing no $HClO_4$.

It has been reported [1] that when the biphase system consisting of a 0.05 mol litre^{-1} solution of DEHP in decane and a 6 M aqueous solution of HNO_3 and containing 1.04×10^{-6} mol litre^{-1} of Bk(IV) and 3.6×10^{-3} mol litre^{-1} of Ce(III) is exposed to α-radiation from ^{244}Cm, Bk(IV) is formed and passes to the organic phase. The maximum degree of oxidation, equal to ~30%, is achieved when the radiation dose is ~360 kGy (the dose rate is ~1.6 Gy s^{-1}). The average G[Bk(IV)] value is ~0.01 ion (100 eV)$^{-1}$.

In 6 M HNO_3, e^-_{aq} and H are converted into NO_2 and then into HNO_2, and the latter reacts with hydrogen peroxide. The OH

radicals react with NO_3^- and HNO_3 to give NO_3 radicals. The latter oxidise Ce(III). The resulting Ce(IV) enters into the reactions with HNO_2 and Bk(III). After that, the reduction of Bk(IV) and its transfer into the organic phase compete with each other. Since the potential of the Bk(IV)/Bk(III) pair decreases, Bk(IV) does not react with HNO_2 in the organic phase.

The stability of Bk(IV) in a solution of perchloric acid exposed to α-particles emitted by ^{244}Cm has been studied.[181] According to our calculations, at $[HClO_4] = 1-5$ M, the $G[-Bk(IV)]$ values vary from 4.2 to 5.1 ion $(100\ eV)^{-1}$. At higher concentrations of the acid, the yields increase. As noted above, the theoretical yield for α-radiolysis in a 1–5 M solution of $HClO_4$ is 3.0 ion $(100\ eV)^{-1}$. The higher values obtained experimentally are caused most probably by the presence of impurities introduced into the solution together with curium.

A study[182] has been devoted to the behaviour of Bk(IV) in solutions of nitric acid under the action of β- and α-radiation (^{244}Cm was used as the source of α-radiation). The reduction of Bk(IV) was found to obey zero-order kinetics. Depending on the concentrations of HNO_3 and Bk(IV) and also on the dose rate, the $G[-Bk(IV)]$ values vary from 8.5 to 13.5 ion $(100\ eV)^{-1}$. The theoretical value should be 4.5–5.5 ion $(100\ eV)^{-1}$. Higher values are achieved due to the presence of impurities.

3. Solutions of californium ions

The formation of Cf(II) upon interaction of e_{aq}^- with Cf(III) in a deaerated solution of californium(III) containing *tert*-butyl alcohol (pH 5.1–5.3) has been detected by pulse radiolysis.[33] The rate constant measured in this study is presented in Table 3. It was found that Cf(II) is responsible for an absorption band with a maximum at 270 nm (the molar extinction coefficient at this wavelength is equal to 50 $m^2\ mol^{-1}$). The consumption of Cf(II) occurs according to first-order kinetics with a rate constant of $7 \times 10^4\ s^{-1}$. In solutions saturated with N_2O, the formation of Cf(IV) was not detected.

Two studies have been devoted to the reduction of $^{249}Cf(IV)$, bound into a complex with $P_2W_{17}O_{61}^{10-}$ induced by its own α-radiation in the presence of $S_2O_8^{2-}$ (see Ref. 1). At the beginning of the process [before ~50% of Cf(IV) is reduced], its rate does not depend on the concentration of Cf(IV), *i.e.* the reaction has the zero order; then the rate decreases and starts to depend on [Cf(IV)]. Calculation of $G[-Cf(IV)]$ based on the results of these studies leads to a value of 32.8 ion $(100\ eV)^{-1}$. Evidently, this high yield is due to impurities.

It has been found[175] that Cf(IV) bound into a complex with $P_2W_{17}O_{61}^{10-}$ is reduced in α-radiolysis, the reduction yield being 7.5–31 ion $(100\ eV)^{-1}$ in the pH range of 2.5–6.1 and at a concentration of the phosphotungstate of 0 to 6.1×10^{-3} mol $litre^{-1}$. The high yields are apparently due to the presence of impurities.

IX. Conclusion

The above consideration indicates that substantial progress has been achieved in the chemistry of aqueous solutions of actinides. Radiolytic transformations of uranium, neptunium, plutonium and americium ions induced by γ- or α-radiation in aqueous solutions under various conditions have been studied in detail; in many cases, the mechanisms of these transformations have been identified. Interesting data about the influence of ionising radiation on aqueous solutions of berkelium ions have been obtained. The first results on the radiolysis of solutions of californium are available. The rate constants for many reactions between actinide ions and the primary products of radiation-induced decomposition of water and with inorganic free radicals (SO_4^-, NO_3, CO_3^-, *etc.*) have been measured using the method of pulse radiolysis. Short-lived intermediates of a number of redox reactions of actinide ions in irradiated aqueous solutions have been identified and studied. A procedure for radiation-induced synthesis of heptavalent neptunium, plutonium and americium has been developed.

However, there are problems to be solved in this field of radiation chemistry. Some of them are formulated below. Note that this list is incomplete, but it points to possible lines of subsequent research in this practically important field of science.

Firstly, radiolysis of aqueous solutions of actinides in nitric acid still remains little investigated. This is mainly due to the fact that radiolytic transformations of nitric acid itself are not completely clear. The foregoing can be illustrated, for example, by the fact that the published values for the molar extinction coefficient of the NO_3 radical, which is among the major intermediate species in the radiolysis of this acid, differ by factors of 4–5 (see, for example, Refs 78 and 183).

Secondly, actinide ions undergo radiolytic transformations induced by their own α-radiation. However, no data about the yields of hydrated electrons in α-radiolysis can be found in the literature, which hampers in some cases interpretation of the results obtained.

Thirdly, the reactivity of actinide ions towards organic free radicals has not been adequately studied. This information would be especially important for describing and predicting the radiolytic behaviour of these ions, for example, in extraction systems used to process irradiated nuclear fuel.

Fourthly, additional investigations of the radiolytic transformations of actinide ions in biphase systems are needed. This would be of interest for the technologies of separation and isolation of radionuclides from industrial solutions.

Fifthly, radiolysis of alkaline aqueous solutions of actinides has been studied only recently. The corresponding studies are of interest in view of the target-directed disposal of highly radioactive alkaline wastes stored in some nuclear centres. In this connection, it should be specially emphasised that it would be expedient to study the influence of ionising radiation on the solubility of plutonium hydroxides in alkaline solutions.

Finally, the problem of the influence of organic impurities on the radiolysis of aqueous solutions of actinides still remains acute. This refers, first of all, to the use of curium as an internal source of radiation. We repeatedly mentioned in the review that the presence of such impurities leads to increased radiation yields. Therefore, development of special methods for the purification of the samples of α-emitters prior to their introduction into solutions and employment of the external irradiation technique (for example, as was done in the 50–60s for the radiolysis of aqueous solutions under the action of α-particles emitted by ^{210}Po) are urgent tasks.

References

1. A K Pikaev, V P Shilov, V I Spitsyn *Radioliz Vodnykh Rastvorov Lan-tanidov i Aktinidov* (Radiolysis of Aqueous Solutions of the Lanthanides and Actinides) (Moscow: Nauka, 1983)
2. A K Pikaev, S A Kabakchi, I E Makarov, B G Ershov *Impul'snyi Radioliz i Ego Primeneniya* (Pulse Radiolysis and Its Applications) (Moscow: Atomizdat, 1980)
3. A K Pikaev *Sovremennaya Radiatsionnaya Khimiya. Osnovnye Polozheniya. Eksperimental'naya Tekhnika i Metody* (Modern Radiation Chemistry. Main Principles. Experimental Technique and Methods) (Moscow: Nauka, 1985)
4. M V Vladimirova *Radiatsionnaya Khimiya Aktinoidov* (Radiation Chemistry of the Actinides) (Moscow: Energoatomizdat, 1983)
5. A K Pikaev, S A Kabakchi, in *Reaktsionnaya Sposobnost' Pervichnykh Produktov Radioliza Vody. Spravochnik* (Reactivity of the Primary Products of Radiolysis of Water. Handbook) (Moscow: Energoizdat, 1982)
6. A K Pikaev *Sovremennaya Radiatsionnaya Khimiya. Radioliz Gazov i Zhidkostei* (Modern Radiation Chemistry. Radiolysis of Gasses and Liquids) (Moscow: Nauka, 1986)
7. M V Vladimirova *Adv. Chem. Ser.* **81** 280 (1968)
8. W G Burns, H E Sims *J. Chem. Soc., Farad. Trans. 1* **77** 2803 (1981)
9. A K Pikaev *Radiat. Phys. Chem.* **22** 241 (1983)
10. S Gordon, J C Sullivan, A B Ross *J. Phys. Chem. Ref. Data* **15** 1357 (1986)

11. A K Pikaev, A V Gogolev, V P Shilov, A M Fedoseev *Isotopenpraxis* **26** 465 (1990)
12. A K Pikaev, A V Gogolev, V P Shilov, A M Fedoseev *Radiat. Phys. Chem.* **37** 531 (1991)
13. A K Pikaev, A V Gogolev, V P Shilov, A M Fedoseev *Khim. Vys. Energ.* **28** 302 (1994) [a]
14. A M Koulkes-Pujo, D Martin-Rovet, G Folcher *Nouv. J. Chim.* **6** 571 (1981)
15. A V Gogolev, V P Shilov, A M Fedoseev, A K Pikaev *Radiokhimiya* **32** 121 (1990) [b]
16. J H Baxendale, E M Fielden, J P Keene *Proc. R. Soc., London, A Math. Phys. Sci.* **286** 320 (1965)
17. J C Sullivan, S Gordon, D Cohen, W Mulac, K H Schmidt *J. Phys. Chem.* **80** 1684 (1976)
18. R K Broszkiewicz, B Vojnovic, B D Michael *Radiat. Phys. Chem.* **37** 443 (1991)
19. R K Broszkiewicz, B Vojnovic, B D Michael *Radiat. Phys. Chem.* **39** 137 (1992)
20. K Nash, W Mulac, M Noon, S Fried, J C Sullivan *J. Inorg. Nucl. Chem.* **43** 897 (1981)
21. W A Mulac, S Gordon, K H Schmidt, D Wester, J C Sullivan *Inorg. Chem.* **23** 1639 (1984)
22. A K Pikaev, V P Shilov, A M Fedoseev *Dokl. Akad. Nauk SSSR* **260** 1407 (1981) [c]
23. A K Pikaev, V P Shilov, A M Fedoseev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1947 (1980) [d]
24. A K Pikaev, M P Mefod'eva, N N Krot, V I Spitsyn *Khim. Vys. Energ.* **7** 505 (1973) [a]
25. A K Pikaev, M P Mefodjeva, F A Zakharova, V P Shilov, N N Krot, A D Gel'man, V I Spitsyn *J. Inorg. Nucl. Chem. Suppl.* 95 (1978)
26. K H Schmidt, S Gordon, M Thompson, J C Sullivan, W A Mulac *Radiat. Phys. Chem.* **21** 321 (1983)
27. A K Pikaev, M P Mefod'eva, N N Krot, V I Spitsyn *Izv. Akad. Nauk SSSR, Ser. Khim.* 2847 (1974) [d]
28. K H Schmidt, S Gordon, R C Thompson, J C Sullivan *J. Inorg. Nucl. Chem.* **42** 611 (1980)
29. A V Gogolev, V P Shilov, A M Fedoseev, A K Pikaev *Izv. Akad. Nauk SSSR, Ser. Khim.* 28 (1990) [d]
30. S Gordon, W A Mulac, K H Schmidt, R K Sjoblom, J C Sullivan *Inorg. Chem.* **17** 294 (1978)
31. A K Pikaev, V P Shilov, V I Spitsyn *Izv. Akad. Nauk SSSR, Ser. Khim.* 2840 (1976) [d]
32. J C Sullivan, K H Schmidt, L R Morss, C G Pippin, C Williams *Inorg. Chem.* **27** 587 (1988)
33. J C Sullivan, L R Morss, K H Schmidt, W A Mulac, S Gordon *Inorg. Chem.* **22** 2338 (1983)
34. J J Katz, G T Seaborg, L R Morss (Eds), in *The Chemistry of the Actinide Elements* Vol. 2 (London: Chapman and Hall, 1986) p. 1143
35. G A Simakin, Yu F Volkov, G I Visyashcheva, I I Kapshukov, P F Baklanova, G N Yakovlev *Radiokhimiya* **16** 859 (1974) [b]
36. A M Fedoseev, V F Peretrukhin, N N Krot *Dokl. Akad. Nauk SSSR* **244** 1187 (1979) [c]
37. 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* (The Heptavalent State of Neptunium, Plutonium, and Americium) (Moscow: Nauka, 1977)
38. G A Simakin *Radiokhimiya* **19** 518 (1977) [b]
39. V Ya Frenkel', I A Lebedev, P L Khizhnyak, B F Myasoedov *Radiokhimiya* **27** 405 (1985) [b]
40. E J Hart, M Anbar *The Hydrated Electron* (Translated into Russian; Moscow: Atomizdat, 1973)
41. V P Shilov, A K Pikaev *Khim. Vys. Energ.* **16** 468 (1982) [a]
42. A V Gogolev, V P Shilov, A M Fedoseev, A K Pikaev *Radiokhimiya* **32** 123 (1990) [b]
43. A V Gogolev, V P Shilov, A M Fedoseev, A K Pikaev *Khim. Vys. Energ.* **25** 472 (1991) [a]
44. V P Shilov, A V Gogolev, A M Fedoseev, A K Pikaev *Khim. Vys. Energ.* **28** 114 (1994) [a]
45. D Golub, H Cohen, D Meyerstein *J. Chem. Soc., Dalton Trans.* 641 (1985)
46. V P Shilov, A K Pikaev, A M Fedoseev *Khim. Vys. Energ.* **16** 89 (1982) [a]
47. A V Gogolev, V P Shilov, A M Fedoseev, I E Makarov, A K Pikaev *Radiokhimiya* **30** 761 (1988) [b]
48. V P Shilov, A M Fedoseev, A K Pikaev *Izv. Akad. Nauk SSSR, Ser. Khim.* 940 (1982) [d]
49. A V Gogolev, V P Shilov, A M Fedoseev, A K Pikaev *Izv. Akad. Nauk SSSR, Ser. Khim.* 456 (1986) [d]
50. V P Shilov, A M Fedoseev, A K Pikaev *Radiokhimiya* **27** 127 (1985) [b]
51. Ch Lierse, K H Schmidt, J C Sullivan *Radiochim. Acta* **44/45** 71 (1988)
52. A K Pikaev, V P Shilov, V I Spitsyn *Dokl. Akad. Nauk SSSR* **232** 387 (1977) [c]
53. A V Gogolev, V P Shilov, A K Pikaev *Izv. Akad. Nauk SSSR, Ser. Khim.* 20 (1989) [d]
54. A K Pikaev, V P Shilov *Izv. AN SSSR. Ser. Khim.* 2136 (1978)
55. V M Berdnikov *Zh. Fiz. Khim.* **47** 2753 (1973) [e]
56. V S Koltunov *Kinetika Reaktsii Aktinoidov* (Kinetics of Actinide Reactions) (Moscow: Atomizdat, 1974)
57. P K Bhattacharyya, R D Saini *Radiat. Phys. Chem.* **13** 57 (1979)
58. P K Bhattacharyya, R D Saini, P B Ruikar *Int. J. Chem. Kinet.* **14** 1219 (1982)
59. A J Elliot, S Radamshi, J Pika *Can. J. Chem.* **64** 314 (1986)
60. V S Koltunov, I A Kulikov, V I Marchenko, A S Milovanova *Radiokhimiya* **22** 833 (1980) [b]
61. N N Krot, L G Shuiskaya *Radiokhimiya* **13** 79 (1971) [b]
62. A S Ghosh Mazumdar, S Vaidyanathan *Radiochim. Acta* **19** 165 (1973)
63. A V Gogolev, V P Shilov, A K Pikaev *Mendeleev Commun.* 127 (1996)
64. A V Gogolev, V P Shilov, A K Pikaev *Khim. Vys. Energ.* **30** 255 (1996) [a]
65. I G Tananaev, V I Dzyubenko *Radiokhimiya* **30** 842 (1988) [b]
66. K Nash, M E Noon, S Fried, J C Sullivan *J. Inorg. Nucl. Chem. Lett.* **16** 33 (1980)
67. T W Newton, F B Baker *J. Phys. Chem.* **60** 1417 (1956)
68. A Ekstrom, A McLaren *J. Inorg. Nucl. Chem.* **34** 1009 (1972)
69. A S Ghosh Mazumdar, P R Natarajan, S Vaidyanathan *J. Inorg. Nucl. Chem.* **32** 3363 (1970)
70. V S Koltunov, I A Kulikov, N V Kermanova, L K Nikishova *Radiokhimiya* **23** 462 (1981) [b]
71. S M Woods, A Cain, J C Sullivan *J. Inorg. Nucl. Chem.* **36** 2605 (1974)
72. P Wardman *J. Phys. Chem. Ref. Data* **18** 1637 (1989)
73. D M Stanbury *Adv. Inorg. Chem.* **33** 69 (1989)
74. R E Huie, C L Clifton, P Neta *Radiat. Phys. Chem.* **38** 477 (1991)
75. A V Gogolev, V P Shilov, A M Fedoseev, A K Pikaev *Mendeleev Commun.* 155 (1993)
76. A V Gogolev, I E Makarov, A K Pikaev, in *Proceedings of the VIth Tihany Symposium on Radiation Chemistry* (Ed P Hedvig) (Budapest: Akademia Kiado, 1987) p. 161
77. A V Gogolev, A M Fedoseev, A K Pikaev *Khim. Vys. Energ.* **21** 478 (1987) [a]
78. Y Katsumura, P Y Jiang, R Nagaishi, T Oishi, K Ishigure, Y Yoshida *J. Phys. Chem.* **95** 4435 (1991)
79. Ch Lierse, J C Sullivan, K H Schmidt *Inorg. Chem.* **26** 1408 (1987)
80. H D Burrows, J D Pedrosa de Jesus *J. Photochem.* **5** 269 (1976)
81. A V Gogolev, A M Fedoseev, in *Tez. Dokl. I Moskovskoi Konferentsii po Radiokhimii* (Abstracts of Reports at the First Moscow Conference on Radiochemistry) (Moscow: Institute of Physical Chemistry of Academy at Sciences of the USSR, 1986) p. 23
82. A V Gogolev, V P Shilov, A M Fedoseev, I E Makarov, A K Pikaev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1248 (1987) [d]
83. R D Saini, P K Bhattacharyya *Radiat. Phys. Chem.* **27** 189 (1986)
84. D Meisel, G Czapski, A Samuni *J. Am. Chem. Soc.* **95** 4148 (1973)
85. D Meisel, Y A Ilan, G Czapski *J. Phys. Chem.* **78** 2330 (1974)
86. A V Gogolev, V P Shilov, A K Pikaev *Radiokhimiya* **31** 124 (1989) [b]
87. A K Pikaev, V P Shilov, V I Nikolaevskii, N N Krot, V I Spitsyn *Radiokhimiya* **19** 720 (1977) [b]
88. A V Gogolev, V P Shilov, A K Pikaev *Khim. Vys. Energ.* **30** 388 (1996) [a]
89. A V Gogolev, V P Shilov, A M Fedoseev, A K Pikaev *Khim. Vys. Energ.* **28** 94 (1994) [a]
90. C C Pippin, G R Choppin, D Meisel, J C Sullivan *J. Less-Common Met.* **149** 193 (1989)
91. A V Gogolev, V P Shilov, A M Fedoseev, A K Pikaev *Khim. Vys. Energ.* **28** 402 (1994) [a]
92. J Teply, I Janovsky, R Mehnert, O Brede *Radiat. Phys. Chem.* **12** 169 (1980)
93. M L Hyder *Radiat. Eff.* **1** 191 (1969)
94. S N Guha, P N Moorthy, K N Rao *Radiat. Phys. Chem.* **29** 425 (1987)
95. G V Buxton, C L Greenstock, W P Helman, A B Ross *J. Phys. Chem. Ref. Data* **17** 513 (1988)

96. R Sankar, P K Bhattacharyya, in *International Symposium on Radiochemistry and Radiation Chemistry. Plutonium 50 Years. Preprints* (Bombay: BARC, 1991) p. RC 25/1-RC 25/2
97. M V Vladimirova *Radiokhimiya* **37** 458 (1995) [b]
98. L Salomon, E Loper-Menehere *Report ETR-182* (Mol, Belgium: European Company for Chemical Processing of Irradiated Fuel, 1966)
99. M V Vladimirova *Radiokhimiya* **35** 112 (1993) [b]
100. R D Saini, P K Bhattacharyya *Radiat. Phys. Chem.* **29** 375 (1987)
101. N N Andreichuk, A A Frolov, V Ya Vasil'ev *Radiokhimiya* **29** 417 (1987) [b]
102. V P Shilov, Yu K Gusev, A K Pikaev, E S Stepanova, N N Krot *Radiokhimiya* **21** 611 (1979) [b]
103. A V Gogolev, V P Shilov, A M Fedoseev, A K Pikaev *Khim. Vys. Energ.* **28** 558 (1994) [a]
104. M Kozik, L C W Baker *J. Am. Chem. Soc.* **21** 7604 (1990)
105. M V Vladimirova *Radiokhimiya* **24** 473 (1982) [b]
106. I A Kulikov, A S Milovanova, M V Vladimirova *Radiokhimiya* **23** 584 (1981) [b]
107. K V Rotmanov, N N Andreichuk, V Ya Vasil'ev *Radiokhimiya* **37** 38 (1995) [b]
108. A A Frolov, N N Andreychuk, K V Rotmanov, L M Frolova, V Ya Vasiliev *J. Radioanal. Nucl. Chem. Artic.* **143** 433 (1990)
109. L M Frolova, A A Frolov, V Ya Vasil'ev *Radiokhimiya* **26** 108 (1984) [b]
110. V Ya Vasil'ev, N N Andreichuk, L M Frolova, A A Frolov, K V Rotmanov *Radiokhimiya* **27** 327 (1985) [b]
111. M V Vladimirova *J. Radioanal. Nucl. Chem. Artic.* **143** 445 (1990)
112. M V Vladimirova *Radiokhimiya* **36** 63 (1994) [b]
113. M V Vladimirova *Radiokhimiya* **37** 44 (1995) [b]
114. M V Vladimirova *Radiokhimiya* **37** 446 (1995) [b]
115. M V Vladimirova *Radiokhimiya* **37** 453 (1995) [b]
116. M V Vladimirova, D A Fedoseev, L A Artemova *Radiokhimiya* **38** 80 (1996) [b]
117. H B Silber, H Nitsche, R Gatti, H Gehmecher, G Feige, J Bucher, N Edelstein *Radiochim. Acta* **66/67** 15 (1994)
118. A K Pikaev, V P Shilov, N N Krot, A D Gel'man, V I Spitsyn *Izv. Akad. Nauk SSSR, Ser. Khim.* 1199 (1969) [d]
119. A K Pikaev, V P Shilov, N N Krot, A D Gel'man, V I Spitsyn *Dokl. Akad. Nauk SSSR* **190** 387 (1970) [c]
120. A K Pikaev, A V Gogolev, S V Kryutchkov, V P Shilov, V N Chulkov, L I Belyaeva, L N Astafurova *Report WHC-EP-0901* (Richland, WA, USA: Westinghouse Hanford Company, 1996)
121. A V Gogolev, V P Shilov, A K Pikaev *Khim. Vys. Energ.* (1997) (in the press) [a]
122. A V Gogolev, V P Shilov, A K Pikaev *Mendeleev Commun.* 8 (1997)
123. M Pages *J. Chim. Phys., Phys. Chim. Biol.* **59** 63 (1962)
124. M S Nagar, P R Natarajan *Radiat. Phys. Chem.* **30** 169 (1987)
125. M V Vladimirova, A A Ryabova, O A Sosnovskii *Radiokhimiya* **22** 679 (1980) [b]
126. M V Vladimirova, I A Kulikov, O A Sosnovskii, A A Ryabova *At. Energ.* **51** 55 (1981)
127. M V Vladimirova *Radiokhimiya* **27** 311 (1985) [b]
128. Z R Turel, P R Natarajan *Lanthanide Actinide Res.* **3** 87 (1989 – 1990)
129. M V Vladimirova *Radiokhimiya* **23** 412 (1981) [b]
130. G P Tkhorzhnitskii, G A Terekhov, G F Egorov, V I Medvedovskii, V B Shevchenko, E V Renard *Radiokhimiya* **17** 724 (1975)
131. G P Tkhorzhnitskii, G F Egorov *Radiokhimiya* **27** 194 (1985) [b]
132. M V Vladimirova, O A Sosnovskii *Radiokhimiya* **22** 662 (1980) [b]
133. M V Vladimirova, I A Kulikov, O A Sosnovskii, L K Nikishova *Radiokhimiya* **24** 332 (1982) [b]
134. V F Kositsyn, A E Konyaev *Radiokhimiya* **31** 9 (1989) [b]
135. K Büppelman, J I Kim, Ch Lierse *Radiochim. Acta* **44/45** 65 (1988)
136. K Büppelman, S Magirius, Ch Lierse, J I Kim *J. Less-Common Met.* **122** 329 (1986)
137. J I Kim, Ch Lierse, K Büppelman, S Magirius *Mater. Res. Soc. Symp. Proc.* **84** 603 (1986)
138. I Pashalidis, J I Kim, Ch Lierse, J C Sullivan *Radiochim. Acta* **60** 99 (1993)
139. M V Vladimirova *Radiokhimiya* **22** 686 (1980) [b]
140. N N Andreichuk, K V Rotmanov, A A Frolov, V Ya Vasil'ev *Radiokhimiya* **26** 94 (1984) [b]
141. N N Andreichuk, V Ya Vasil'ev, N B Vysokoostrovskaya, V M Kalashnikov, V I Karasev, E A Karelin, V B Mishinev, V M Nikolaev, S V Osipov *Radiokhimiya* **18** 89 (1976) [b]
142. N N Andreichuk, K V Rotmanov, A A Frolov, V Ya Vasil'ev *Radiokhimiya* **29** 412 (1987) [b]
143. N N Andreychuk, A A Frolov, K V Rotmanov, V Ya Vasiliev *J. Radioanal. Nucl. Chem. Artic.* **143** 427 (1990)
144. M V Vladimirova, E A Golub' *Radiokhimiya* **30** 547 (1988) [b]
145. M V Vladimirova, E A Golub' *Radiokhimiya* **34** (4) 91 (1992) [b]
146. M V Vladimirova *Radiokhimiya* **34** (6) 89 (1992) [b]
147. M V Vladimirova *Radiokhimiya* **34** (6) 102 (1992) [b]
148. M V Vladimirova *Radiokhimiya* **34** (6) 116 (1992) [b]
149. M V Vladimirova *Radiokhimiya* **35** (1) 130 (1993) [b]
150. M V Vladimirova *Radiokhimiya* **35** (1) 145 (1993) [b]
151. M V Vladimirova *Radiokhimiya* **35** (5) 126 (1993) [b]
152. K V Rotmanov, N N Andreichuk, V Ya Vasil'ev *Radiokhimiya* **35** (4) 135 (1993) [b]
153. D D Walker, N E Bibler *Report WSRC-RP-1991-1171* (1991)
154. D T Reed *Mater. Res. Soc. Symp. Proc.* **294** 431 (1993)
155. Y Kuno, T Hina, J Masui *J. Nucl. Sci. Technol.* **30** 919 (1993)
156. A V Gogolev, V P Shilov, A K Pikaev *Khim. Vys. Energ.* **31** 179 (1997) [a]
157. F A Zakharova, A K Pikaev, M M Orlova, A D Gel'man, V I Spitsyn *Dokl. Akad. Nauk SSSR* **201** 636 (1971) [c]
158. P K Bhattacharyya, R D Saini *Radiat. Eff. Lett.* **57** 165 (1981)
159. R D Saini, P K Bhattacharyya *Radiat. Phys. Chem.* **23** 509 (1984)
160. C N Delegard *Radiochim. Acta* **41** 11 (1987)
161. V P Shilov, A Yu Garnov, L N Astafurova, N N Krot *Radiokhimiya* **38** 231 (1996) [b]
162. S Magirius, W T Carnell, J I Kim *Radiochim. Acta* **38** 29 (1985)
163. A A Frolov, V M Chistyakov, A S Kornilov, V Ya Vasil'ev *Radiokhimiya* **27** 59 (1985) [b]
164. E A Erin, V V Kopytov, V Ya Vasil'ev, A G Rykov *Radiokhimiya* **23** 727 (1981) [b]
165. A K Pikaev, V P Shilov, N N Krot, V I Spitsyn *Izv. Akad. Nauk SSSR, Ser. Khim.* 951 (1976) [d]
166. J C Sullivan, S Gordon, W A Mulac, K H Schmidt, D Cohen, R Sjoblom *Inorg. Nucl. Chem. Lett.* **12** 599 (1976)
167. P-Y Jiang, Y Katsumura, M Domae, K Ishikawa, R Nagaishi, K Ishigure *J. Chem. Soc., Faraday Trans.* **88** 3319 (1992)
168. 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) [c]
169. A V Anan'ev, V P Shilov *Radiokhimiya* **34** (4) 21 (1992) [b]
170. A S Kornilov, A A Frolov, V Ya Vasil'ev *Radiokhimiya* **27** 54 (1985) [b]
171. A S Kornilov, A A Frolov, V Ya Vasil'ev *Radiokhimiya* **28** 656 (1986) [b]
172. A A Frolov, L M Frolova, V Ya Vasil'ev *Radiokhimiya* **29** 79 (1987) [b]
173. A A Frolov, V M Chistyakov, A S Kornilov, V Ya Vasil'ev *Radiokhimiya* **26** 745 (1984) [b]
174. E A Erin, V V Kopytov, V Ya Vasil'ev *Radiokhimiya* **28** 185 (1986)
175. V M Chistyakov, A A Baranov, P N Karbovnichii, E A Erin, G A Timofeev *Radiokhimiya* **32** (4) 36 (1990) [b]
176. V N Kosyakov, Yu G Davydov *Radiokhimiya* **25** 207 (1983) [b]
177. E A Erin, V M Vityutnev, V V Kopytov, V Ya Vasil'ev *Radiokhimiya* **24** 179 (1982) [b]
178. V I Chepovoi, I A Lebedev, Yu M Kulyako, B F Myasoedov *Radiokhimiya* **22** 658 (1980)
179. M N Litvina, D A Malikov, M S Milyukova, B F Myasoedov *Radiokhimiya* **22** 653 (1980) [b]
180. A A Frolov, V V Kopytov, L M Frolova, V Ya Vasil'ev *Radiokhimiya* **30** 557 (1988) [b]
181. L M Frolova, V M Vityutnev, V Ya Vasil'ev *Radiokhimiya* **28** 27 (1988) [b]
182. L M Frolova, V M Vityutnev, V Ya Vasil'ev *Radiokhimiya* **25** 212 (1982) [b]
183. A K Pikaev, G K Sibirskaya, E M Shirshov, P Ya Glazunov, V I Spitsyn *Dokl. Akad. Nauk SSSR* **215** 645 (1974) [c]

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