Reviews

Short-lived metal clusters in aqueous solutions: formation, identification, and properties

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The formation and properties of short-lived homo- and heteronuclear metal clusters in aqueous solutions were investigated by pulse radiolysis. These species arise in early stages of the aggregation of metal atoms and ions in unusual oxidation states. The conditions favoring the formation of positively charged "magic" clusters and intermediate heterometallic clusters were elucidated.

Key words: metals, unusual oxidation states, nucleation, clusters; sols, colloids; pulse radiolysis, absorption spectra, electron structure.

Short-lived clusters play an important role in chemistry. They arise as intermediates in diverse chemical reactions, and their detection and study of their properties is significant for understanding the mechanism of a process. However, the possibility of investigating small clusters,* comprising 2 to 10 atoms, is limited due to their short lifetimes; therefore, experimental methods that enable their rapid detection need to be used. The substantial progress in this field is associated with the development of the pulse radiolysis method[1] and its use in the study of the mechanism of reduction of metal ions in aqueous solutions. It has been found (see reviews[2-4]) that reactions of many metal ions with the radical-ion products of water radiolysis (hydrated electrons, hydrogen atoms, and hydroxyl radicals) occur as one-electron reduction or oxidation, yielding metal atoms or ions in intermediate oxidation states. Under specially selected conditions in which one-electron reduction of metal ions occurs predominantly, the subsequent aggregation of the resulting atoms and ions gives more or less complex small clusters, and then quasimetallic particles; at the final stage, metal sols are formed. Pulse radiolysis makes it possible to perform unique experiments in colloidal chemistry, namely, to follow all the intermediate steps of the metal phase nucleation in a homogeneous medium. The sequential cluster aggregation allows one to identify the gradual transition from the atomic and molecular properties of small particles to the bulk metal properties.

In this review, the results of pulse radiolysis studies of the formation and properties of short-lived clusters and metal nanoparticles in aqueous solutions are sur-

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* The term "cluster" is used widely in modern chemistry. Most often, it is taken to mean agglomerates of metal atoms consisting of three or more atoms. In this review, as in the majority of studies cited in it, the term small clusters is used in reference to species comprising two or more metal atoms.

veyed. The attempt is made to elucidate the conditions of the formation of clusters with a "magic" composition and structure, which are highly kinetically stable and which are formed preferably compared to a large number of formally possible species during the reductive nucleation of a metal in an aqueous solution. The data concerning the formation of mixed clusters of two metals under certain conditions and on the subsequent reactions involving these species are also presented.

Simple clusters and metal nucleation

Clusters consisting of atoms and ions of one metal, i.e., homonuclear, will be referred to as simple clusters. These species result from reduction of metal ions in aqueous solutions and precede the formation of the metal phase. To determine the nature of the arising clusters (nuclearity, charge, etc.) by pulse radiolysis, known procedures of kinetic analysis are used, i.e., the effects of the reactant concentration, the ionic strength of the solution, the dose rate in the electron pulse, and some other factors on the reaction route and rates are studied. A substantial contribution to the identification of short-lived species is also made by measurement of the electrical conductivity of irradiated solutions, in addition to optical recording.

Fig. 2. Optical absorption spectra of positively charged silver clusters 20 ms (1), 80 ms (2), and 4 s (3) after a pulse of accelerated electrons. For the solution composition and irradiation conditions, see Fig. 1.
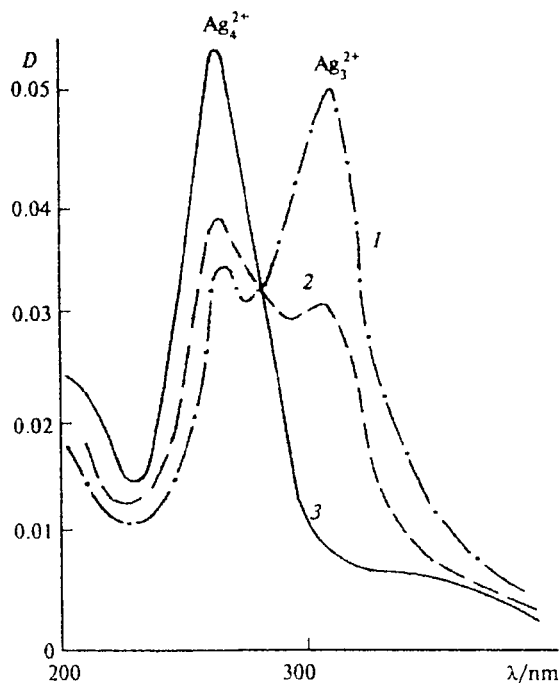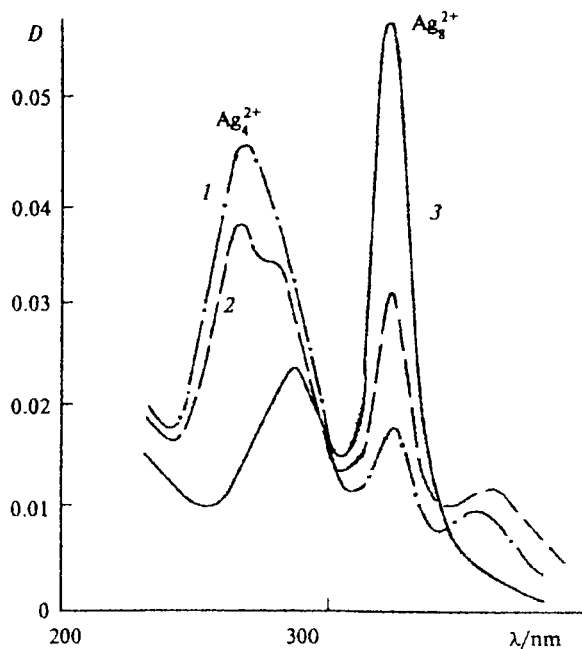

Fig. 1. Optical absorption spectra of positively charged silver clusters 3 μs (1), 27 μs (2), and 0.4 ms (3) after the action of a pulse of accelerated electrons on an aqueous solution containing $AgClO_4$ ($1 \cdot 10^{-4}$ mol L^{-1}) and Pr^iOH (0.1 mol L^{-1}). The irradiation gives $4 \cdot 10^{-6}$ mol L^{-1} of hydrated electrons and $Me_2C^\cdot OH$ radicals.
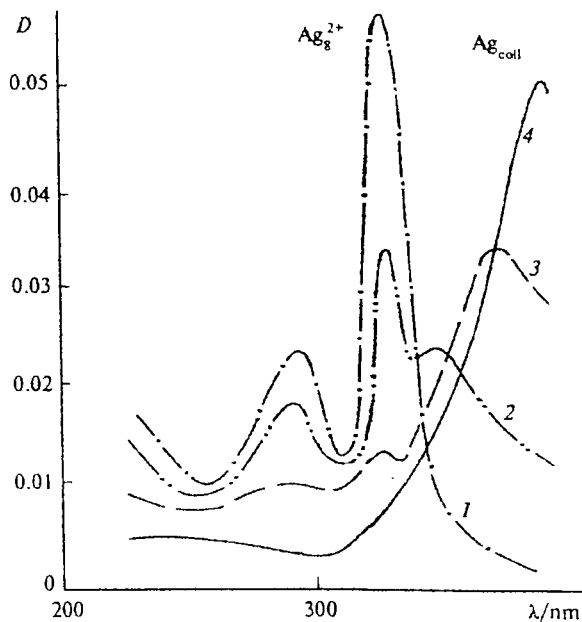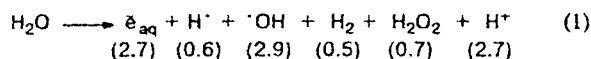

Fig. 3. Optical absorption spectra of positively charged silver clusters and sols 6 s (1), 1 min (2), 5 min (3), and 15 min (4) after a pulse of accelerated electrons. For the solution composition and irradiation conditions, see Fig. 1.

Silver nucleation has been studied by pulse radiolysis in the greatest detail.[5—15] The silver clusters of different complexity, formed in intermediate stages, are responsible for typical optical absorption bands. This metal proves to be an excellent model that allows one to follow the evolution from atom to sol. Figures 1—3 show the successive intermediate stages of this process during the reductive nucleation of silver in an aqueous solution. The concentration of silver ions used in the experiments was much higher than that of reducing species generated by radiation. Under these conditions, only positively charged silver clusters arise in an aqueous solution.

Let us consider this process in more detail. When an aqueous solution containing silver ions and an organic additive (alcohols or HCOONa) is exposed to a pulse of accelerated electrons, species with high reduction potentials are generated. In the case of isopropyl alcohol, these species include hydrated electrons and $Me_2C^{\cdot}OH$ radicals, which are produced in reactions (1) and (2) in approximately equal amounts.

$$H_2O \longrightarrow \overset{-}{e}_{aq} + H^{\cdot} + {}^{\cdot}OH + H_2 + H_2O_2 + H^+ \quad (1)$$
$$ (2.7) \quad (0.6) \quad (2.9) \quad (0.5) \quad (0.7) \quad (2.7)$$

$$Me_2CHOH + {}^{\cdot}OH\,(H^{\cdot}) \longrightarrow Me_2\overset{\cdot}{C}OH + H_2O\,(H_2) \quad (2)$$

For reaction (1), the radiation-chemical yields of the products of water radiolysis per 100 eV of the absorbed energy are given in parentheses. Since the potentials of the hydrated electron and isopropyl radical are −2.9 and −1.4 V, respectively[2—4] and $E^0(Ag^+/Ag^0) = -1.8$ V, only hydrated electrons participate in the reduction of silver ions. They react with silver ions

$$Ag^+ + \overset{-}{e}_{aq} \longrightarrow Ag^0$$
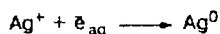
to give atoms, which account for a broad band with a maximum at 360 nm in the optical absorption spectrum.[14] A correlation between the rates at which this band appears and the rates at which the absorption band at 700 nm, due to the hydrated electron, disappears was established by pulse radiolysis. Over a short period after the pulse, the silver atoms are transformed into simple clusters:[15]

$$Ag^0 + Ag^+ \longrightarrow Ag_2^+,$$

$$Ag_2^+ + Ag^+ \longrightarrow Ag_3^{2+}.$$
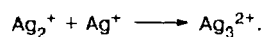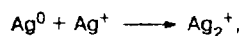
The rates of consumption of silver atoms and the rates of formation of the corresponding clusters are directly proportional to the concentration of the silver ions in the solution. After 3—5 μs, absorption of the Ag_3^{2+} cluster predominates in the optical spectrum of an aqueous deaerated solution of $AgClO_4$ ($1 \cdot 10^{-4}$ mol L^{-1}). The spectrum of this cluster exhibits two optical absorption bands, at 310 and 265 nm (see Fig. 1). It can be seen that disappearance of Ag_3^{2+} is accompanied by the

appearance of an absorption band at 265 nm, which corresponds to a new cluster, Ag_4^{2+}. This cluster is formed by the following scheme:

$$2\,Ag_3^{2+} \longrightarrow Ag_4^{2+} + 2\,Ag^+.$$
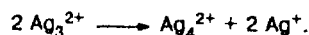
The Ag_4^{2+} cluster proves to be fairly stable; the time it takes for it to disappear entirely is ~1 s. The rates of the decay of this species depend on the ionic strength of the solution. The elementary charge of +2, which corresponds to the composition proposed for this cluster, was calculated from the Brønsted—Bjerrum equation.[14] When Ag_4^{2+} disappears, two new optical absorption bands, at 295 and 325 nm, appear in the spectrum (see Fig. 2). Analysis of the kinetics of the decay of Ag_4^{2+} and the appearance of the above-mentioned absorption bands led to the conclusion[14] that the species formed contains about eight silver atoms; this species was identified as Ag_9^+. According to the quantum-chemical calculations carried out later,[16] the cluster characterized by this type of optical parameters is most likely Ag_8^{2+}.* The rates of formation of this species increase with an increase in the ionic strength of the solution more steeply than the decay of Ag_4^{2+}. The product of the charges of the reacting species, which are precursors of Ag_8^{2+}, is equal to 8±1 (see Refs. 12, 14). This fact can be explained by assuming that the decay of the Ag_4^{2+} species has an intermediate step in which a multicharged cluster is formed, for example
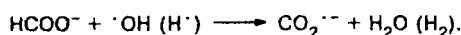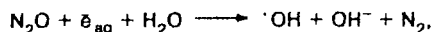
$$2\,Ag_4^{2+} \longrightarrow Ag_8^{4+},$$

$$Ag_8^{4+} + Ag_4^{2+} \longrightarrow Ag_8^{2+} + 4\,Ag^+.$$
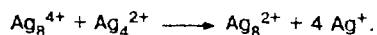
The Ag_8^{2+} cluster is extremely stable in aqueous solution, its lifetime is about 15—30 min.[13] The disappearance of this cluster is accompanied by the appearance of a broad band at 360—370 nm, which belongs to quasimetallic particles (see Fig. 3). The band gradually shifts to the visible region and transforms into an intense band with a maximum at 390 nm, which smoothly drops to the visible region. This band corresponds to silver sols and is due to the light absorption by surface plasmons. The absorption by metal sols is adequately described in terms of the Mie theory or its modifications.[17,18]

Thus, the intermediate steps of reduction (incomplete reduction) in aqueous solutions containing excess silver ions with respect to the concentration of the reducing radical species generated by radiation yield only positively charged and kinetically rather stable clusters (whose lifetimes are considerably longer than that corresponding to the diffusion-controlled reactions). These clusters grow via successive reactions and are gradually transformed into colloidal metal.

Neutral silver clusters were obtained[14] by pulse irradiation of aqueous solutions of silver ions under condi-

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* This was confirmed by direct observations of this cluster by high-resolution electron microscopy (see below).

tions when the concentration of the reducing agents was higher than the concentration of the metal ions present (complete reduction). These conditions ensure almost instantaneous reduction of silver ions to give neutral clusters. Figure 4 shows their optical absorption spectra in an aqueous solution of $AgClO_4$ containing HCOONa and saturated with N_2O. Upon pulse irradiation, the hydrated electrons, hydrogen atoms, and $OH^\cdot$ radicals are transformed into $CO_2^{\cdot-}$ radical anions

$$N_2O + e_{aq} + H_2O \longrightarrow \cdot OH + OH^- + N_2,$$

$$HCOO^- + \cdot OH \ (H^\cdot) \longrightarrow CO_2^{\cdot-} + H_2O \ (H_2).$$

The dose absorbed per pulse was chosen in such a way that the concentration of the $CO_2^{\cdot-}$ radical anions was twice that of the silver ions present in the solution. The reduction potential of the $CO_2^{\cdot-}$ radical anions is -1.9 V,[2—4] which ensures reduction of Ag^+ ions in the reaction

$$Ag^+ + CO_2^{\cdot-} \longrightarrow Ag^0 + CO_2.$$

Under these irradiation conditions, the process of formation of neutral silver clusters predominates. The absorption bands of neutral clusters are rather broad; their optical spectra, unlike those of positively charged clusters, exhibit no well-resolved bands. The clusters were identified based on computer analysis of the kinet-

ics of their sequential growth.[14] These clusters are actually neutral because a change in the ionic strength of the solution has no effect on the kinetics of their formation and decay. It was suggested[14] that the optical absorption of the species arising after 10 μs (bands with maxima at 310 and 340 nm), 250 μs (280 and 330 nm), and 4 ms (370 and 400 nm) belong to Ag_2, Ag_4, and Ag_8, respectively. However, these kinetic calculations were carried out with the assumption that the initial simple silver cluster is the Ag_2^+ ion. Later, it has been found[15] that in reality, this is Ag_3^{2+}; therefore, there are grounds to revise the interpretation proposed previously. It can be assumed that the above-mentioned absorption bands of the intermediate neutral clusters correspond to the following species: Ag_3, Ag_6, and Ag_n with $n > 10$ (e.g., 12—14). The Ag_3 cluster is formed at an early reduction step when recombination reactions are insignificant. Conversely, when the Ag_6 cluster is formed, the role of these reactions is crucial, as indicated by the proportional increase in the rates of their formation following an increase in the dose absorbed per pulse. The Ag_n cluster appears in a more complex process. Later, we shall discuss its structure and the structure of Ag_6 regarding the correspondence of their structures to the structures of "magic" clusters. Neutral clusters, unlike positively charged ones, are kinetically unstable and the reactions in which they disappear are controlled by diffusion. About 40 ms after the pulse of accelerated electrons, the agglomeration of these species ends with the formation of colloidal metal.

The spectra of positively charged clusters in water contain intense narrow absorption bands. Their extinction coefficients (ε) are close and amount to $\sim 2 \cdot 10^4$ L mol^{-1} cm^{-1}.[14] The absorption bands of neutral clusters are markedly broader and less intense. This is due to the greater number of valence electrons, fuller filling of molecular orbitals, and the occurrence of a large number of electron transitions. In the case of large clusters, the compositions of both free and occupied
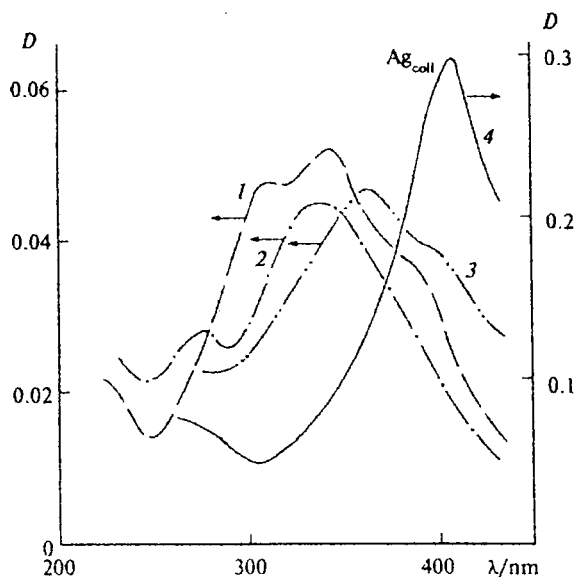
Fig. 4. Optical absorption spectra of neutral silver clusters and sols 10 μs (1), 250 μs (2), 4 ms (3), and 40 ms (4) after the action of a pulse of accelerated electrons on an aqueous solution containing $AgClO_4$ ($2 \cdot 10^{-5}$ mol L^{-1}), HCOONa ($1 \cdot 10^{-2}$ mol L^{-1}), and N_2O ($2.5 \cdot 10^{-2}$ mol L^{-1}). The irradiation gives $4 \cdot 10^{-5}$ mol L^{-1} of the $CO_2^{\cdot-}$ radical anions.

Table 1. Characteristics of positively charged silver clusters in aqueous solutions

Cluster	Configuration	r(Ag—Ag) /au	Optical transition	λ_{max}/nm	
				theor.	exp.
Ag_3^{2+}	linear	4.6—5.0	$1s_g—1p_u$	260—285	265
			$1s_g—2s_g$	275—320	310
			$1s_g—1s_u$	540—720	—
Ag_4^{2+}	square	4.8—5.6	$1a_{1g}—1a_{1u}$	270—293	265
			$1a_{1g}—1e_g$	335—390	—
Ag_8^{2+}	cube	5.0—5.6	$1a_{1g}—1t_{2g}$	230—275	295
			$1t_{1u}—2a_{1g}$	300—320	325
			$1t_{1u}—1e_g$	420—440	—
			$1t_{1u}—1t_{2g}$	480—600	—
Ag_{14}^{2+}	fcc*	5.4	12 transitions	240—520	360—380

* Face-centered cubic.

orbitals are mixed,[16] the density of states substantially increases, and the individual electronic transitions coalesce to give broad blurred bands.

Table 1 presents the results of theoretical calculations of the optical transitions for positively charged silver clusters,[16] which can be compared with experimental results. Good agreement is found only for structures presented in Table 1. Calculations for other configurations of the same clusters do not lead to a satisfactory agreement with the experimental λ_{max} values of optical transitions.

It should be noted that the quantum-chemical calculations[16] were carried out in the approximation of "naked" clusters, i.e., without allowance for their hydration. This was due not only to the lack of information on the possible structure of the solvation shell of the clusters but also to the fact that these calculations are very complicated. Comparison of the calculated and experimental spectra of the clusters in water or in an inert gas matrix demonstrates that, first, the experimental spectrum contains bands corresponding to symmetry-forbidden electron transitions, and, second, these spectra, especially those recorded in aqueous solutions, exhibit bands corresponding to short-wave transitions. Both findings indicate that the clusters interact with water molecules. The former is due to the fact that the symmetry of the aquated cluster is lower than that of the "naked" one, while the latter finding is due to the fact that water molecules interact with the lowest vacant molecular levels and are relatively inactive during the electron transfer. Therefore, no substantial difference is observed between the structures of optical transitions for "naked" and aquated clusters.

The results of our studies demonstrate that of the enormous number of formally possible positively charged silver clusters containing different numbers and ratios of ions and atoms and having different structures, only few clusters are actually formed. These are Ag_3^{2+}, Ag_4^{2+}, and Ag_8^{2+} species, which are precursors of the colloidal metal. The latter two clusters are kinetically rather stable. These clusters can be defined as "magic."*

The question arises of what are the common features of "magic" clusters that make the formation of exactly these species preferred? In our opinion, the property that distinguishes the "magic" clusters from other clusters is that their structural and electronic properties correspond to those of bulk metal. The unit cell of silver metal has a face-centered cubic (fcc) lattice, and the number of s-electrons per Ag—Ag bond is equal to 0.5. It can be seen from the data listed in Table 1 that the same number of electrons falls on one Ag—Ag bond in

positively charged clusters. Apparently, this is an essential requirement of a "magic" cluster. In addition, it is significant that the cluster configuration should correspond to a structural fragment of the fcc lattice of the metal and the number of atoms in the cluster and its charge should be even. In addition, the charge should not be great because this would increase electron affinity and the susceptibility of the cluster for reduction and, hence, would decrease the cluster stability. These requirements are not fully met only for the first and the simplest cluster, Ag_3^{2+}, which contains one silver atom (has an unpaired electron) and, therefore, it is kinetically highly active. The Ag_8^{2+} cluster is the immediate precursor of the colloidal silver formed. The decay of these species is accompanied by the formation of quasimetallic and then colloidal silver. Moreover, it was found[20] that when silver sols are exposed to light in their absorption region ($\lambda = 366$ nm), they undergo fragmentation to give the same Ag_8^{2+} clusters. Thus, these clusters are the structural units that form colloidal silver and are formed from colloidal silver in an aqueous solution. By now, direct evidence has been obtained confirming that the cluster that we identify as Ag_8^{2+} actually does consist of eight silver atoms. Previously it had been known[21] that this cluster is formed upon chemical or radiation-induced decomposition of clusterites (linear silver clusters stabilized on a polyacrylic acid chain in a aqueous solution). A species containing eight silver atoms was actually detected among the clusterite decomposition products by scanning tunneling microscopy.[22] More precisely, only seven atoms were observed but, in the opinion of the authors of Ref. 22, the geometric structure of the cluster in question suggests that it contains one more, invisible silver atom covered by other atoms. Thus, there are enough grounds to believe that this process affords a magic cluster containing eight silver atoms, which we identify as Ag_8^{2+}.

In conformity with the formulated requirements of stable positively charged silver clusters, the Ag_{14}^{2+} cluster could be next in order of complexity after Ag_8^{2+}. In fact, this species has a small positive charge and an fcc lattice of the metal, and contains 0.5 electrons per Ag—Ag bond. The quantum theory predicts that this species would exhibit broad absorption in the UV and visible regions due to the high density of optical transitions.[16] Apparently, the broad absorption band with a maximum at 360—370 nm formed in the spectrum can be attributed to this type of species. The gradual shift of this band with the appearance of the typical absorption of colloidal silver (with a maximum at 390 nm) is due to the growth of the quasimetallic particles and transition from atomic and molecular properties to the bulk metal properties.

The high kinetic stability of the positively charged clusters compared to neutral clusters can apparently be attributed to the Coulomb repulsion between them and to the fact that the degree of chemical bond saturation

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* The term "magic," which here refers to small clusters, should be distinguished from the same term used to denote large clusters. According to P. Chini,[19] metal atoms in the latter are packed similarly to those in the bulk metal, forming a polyhedron typical of the crystallites of this metal. The family of "Chini" clusters includes 13-, 55-, 309-, 561-atomic clusters, etc.

in these clusters is equal to that in the metal. The assumption that positively charged silver clusters in aqueous solutions are fragments of the crystal structure of the bulk metal corresponds to the general approach used to describe the configurations of cluster molecules of many metals, which has been widely confirmed in experiments.[19,23—25] However, in some cases, the degree of freedom in the packing of atoms in a cluster is much higher than that in the metal. In fact, neutral clusters are often constructed as a cubooctahedral core with an atom in the center and 12 atoms in the vertices of the polyhedron. Note that the Ag_{13} cubooctahedron obeys in a way the rule that we have established for magic silver clusters, namely, the number of electrons per Ag—Ag bond in this species is 0.5 (if the bonds of the central silver atom are neglected). This rule is fulfilled for the Ag_6 cluster, which is shaped like a tetrahedral bipyramid. It might be suggested that Ag_6 and Ag_{13} are the neutral clusters resulting from the complete reduction of silver ions in aqueous solutions. However, it is doubtful if the Ag_6 clusters, containing an even number of atoms, could be converted into a cluster with an odd number of atoms, Ag_{13}, which has an unpaired electron and, therefore, is kinetically very reactive. The hypothesis that the Ag_6 clusters are converted into the Ag_{12} species with a cubooctahedral structure, which fully conforms to the "magic" rule, 0.5 electrons per Ag—Ag bond, seems more plausible. There are also no grounds for excluding the possible formation of the positively charged cluster Ag_{13}^+ or Ag_{14} with a fcc structure, i.e., the structure of the unit cell of metallic silver, from consideration.

Let us consider the nucleation of silver in terms of the electron configurations of clusters.[16] A necessary condition for cluster recombination is the presence of an s-electron in a partially occupied molecular orbital (MO) with the same type of symmetry.[26] This condition is fulfilled for the Ag_3^{2+} ion (electron configuration $1\sigma^1_g 1\sigma^0_u 1\pi^0_u$) and accounts for its high reactivity. The Ag_4^{2+} cluster has the electron configuration $1a^2_{1g} 1e^0_g$, and the number of electrons per bond is 0.5. It contains two paired electrons on the $1a_{1g}$ level, and the interaction with the $1e^0_g$ MO is symmetry forbidden. Thus, the condition for effective interaction of two cations is not met. This species has a low reactivity, and the rate constant for recombination $(2\cdot10^7$ L mol^{-1} s$^{-1})$ is approximately two orders of magnitude lower than that for the Ag_3^{2+} clusters $(1.3\cdot10^9$ L mol^{-1} s$^{-1})$.[14] Apparently, interaction of the Ag_4^{2+} clusters involves the step of excitation to the $1a^2_{1g} 1e^1_g$ state, which accounts for its low reactivity. The product of recombination of these two cations, Ag_8^{4+}, is relatively unstable due to its large charge and weak Ag—Ag bond. The Ag_8^{2+} cluster formed in the next step has an even charge and 0.5 electrons per Ag—Ag bond. The electron configuration of this cluster, $a^2_{1g} t^4_{1u} t^0_{2g}$, suggests its high stability.

Silver sols are formed upon coalescence of the Ag_8^{2+} clusters. Since the t_{1u} MO is partially occupied, cou-

pling of these clusters is allowed from the symmetry viewpoint. Deceleration of the reaction is due to the repulsion of the positive charges and, possibly, to the consumption of energy for the separation of the paired electrons. Since the enlargement of species should yield the fcc lattice of the bulk metal, it can be suggested that the following process would predominate in the interaction of the Ag_8^{2+} clusters: a silver atom in a vertex of the cube of one cluster gets into the middle of a face of another cube. This gives a unit of an fcc structure, which becomes a nucleus of the arising sol. The optical and electronic properties of these nuclei are close to the properties of the Ag_{14} clusters, whose sequential coalescence or growth permanently bring the atomic and molecular properties of clusters closer to the properties of the condensed metal. The interaction of large clusters involves a steric effect, which retards the reaction and can account for the fact that the process of sol formation takes a lot of time. In fact, the lifetime of the Ag_8^{2+} clusters is measured by tens of minutes;[13] in the presence of some polyelectrolytes (polyphosphates, polyacrylates), fairly stable aqueous solutions of these species have been obtained.[27—31] Their chemical properties had been studied even before the nature of the clusters themselves was determined. Conversely, the presence of sulfate ions in the solution substantially decreases the stability of the Ag_8^{2+} clusters, and their decay is controlled by diffusion.[11—14,32,33] Apparently, under these conditions, extremely unstable neutral species such as Ag_8SO_4 are formed. The neutralization of the cluster charge removes the Coulomb repulsion, which has ensured the stability of the clusters in the aqueous solution. This accounts for the fact that in earlier studies[6—9] dealing with pulse radiolysis of aqueous solutions of Ag_2SO_4 these magic clusters had not been discovered. They were observed[10] only when Ag_2SO_4 was replaced by $AgClO_4$. When this was done, the lifetime of the Ag_8^{2+} clusters increased by 4—5 orders of magnitude. Comprehensive studies of the influence of various factors on the stability of the Ag_8^{2+} clusters and, hence, on the process of sol formation demonstrated[12,13,32,33] that an increase in the ionic strength of the solution or introduction of specifically sorbable (or capable of coordination) anions $(OH^-, SO_4^{2-}, HCOO^-,$ etc.) increases the rates of coagulation of the clusters and, correspondingly, the rates of formation of silver sols by several orders of magnitude. The Ag_8^{2+} cluster possesses reductive properties.[20] It is readily oxidized by oxygen and reduces tetranitromethane to give the $C(NO_2)_3^-$ anion.

It is noteworthy that silver atoms and simple clusters arise upon irradiation of frozen (77 K) aqueous or alcoholic solutions of silver salts[34—38] and also in the presence of silver ions sorbed in a zeolite matrix or some other solids (see, for example, a review[39]). The composition and structure of paramagnetic species $(Ag_2^+, Ag_3^{2+},$ and so on) were studied by ESR spectroscopy. It was shown[38] that heating of aqueous solutions of silver ions containing isopropyl alcohol that have been γ-irradiated

at 77 K is accompanied by reduction of the Ag_4^{2+} cluster by $Me_2C\cdot OH$ radicals to give the species Ag_4^+.

The formation of positively charged clusters with different degrees of complexity is a rather common property of metal ions in unusual oxidation states having an unpaired electron on outer s or p orbitals and a low charge (0 or +1). Thus it was found by pulse radiolysis[40-43] that reduction of thallium ions by hydrated electrons, hydrogen atoms, or alcohol radicals is accompanied by the formation of Tl_2^+ cluster and the product of its dimerization, Tl_4^{2+}. The Cu_2^+ and Cu_4^{2+} clusters result from reduction of chloride complexes of monovalent copper by hydrated electrons.[44] The In_2^+ and In_4^{2+} clusters were discovered[45] upon pulse radiolysis of aqueous solutions of $InClO_4$. In the above examples, as in the case of silver, the formation of positively charged clusters is preceded by the formation of metal atoms. A specific feature of these atoms is the ability to add an additional metal cation at the σ_s bond in the case of silver or copper or at the σ_{sp} bond in the case of indium and thallium. By analogy, it might appear that other ions, for example, Cd^+ and Pb^+, in unusual oxidation states would act as the source of Cd_2^{3+} and Pb_2^{3+} clusters, respectively. The Cd_2^{3+} cluster is an isoelectronic analog of Ag_2^+. The formation of this cluster was observed only under specific conditions, viz., upon γ-irradiation of frozen (77 K) sufficiently concentrated (>1 mol L^{-1}) aqueous solutions of cadmium salts.[46-49] Apparently, stability of the Cd_2^{3+} cluster in the rigid matrix is ensured by its limited mobility and the cage effect. The attempts to detect this cluster in aqueous solutions at room temperature failed.[50] These conditions were more favorable for the appearance of cadmium atom or the Cd_2^{2+} dimer (see Refs. 51 and 52).

All the foregoing is also true for mercury. The Hg_2^{3+} cluster is formed upon low-temperature γ-irradiation of aqueous solutions of mercury salts,[49,53] whereas in liquid aqueous solutions, the Hg_2^{2+} cluster is formed upon recombination of the Hg^+ ions (see Refs. 54 and 55). Note that the Cd_2^{2+} and Hg_2^{2+} clusters have two electrons in the bonding σ_s orbital, unlike the silver, thallium, copper, and indium dimeric clusters, considered above, which contain one electron. This determines the higher stability of the former (the Hg_2^{2+} ion is even a stable form of existence of mercury) in relation to the latter. Complex mercury clusters are formed during the radiation-induced reduction of sufficiently concentrated (>0.1 mol L^{-1}) aqueous solutions of Hg_2^{2+} ions.[56] Under these conditions, after the action of a microsecond pulse of accelerated electrons, an intense absorption band with a maximum at 390 nm and a much weaker band in the 500—600 nm region appear in the optical spectra.

A similar situation is observed for metal atoms and ions having an unpaired electron in the p-orbital. As has already been noted, the Tl^0 and In^0 atoms resulting from reduction of Tl^+ and In^+ ions tend to add metal ions to give the dimers Tl_2^+ and In_2^+, whose subsequent re-

combination affords more complex clusters. The formation of clusters during the radiation-induced reduction of Pb^{2+} ions, which are isoelectronic with thallium ions, follows a different mechanism. Figure 5 illustrates this process induced by an electron pulse in a deaerated aqueous solution of $Pb(ClO_4)_2$ containing isopropyl alcohol. In this and in the subsequent figures, the optical spectra are described in terms of extinction coefficients ($\varepsilon/L\ mol^{-1}\ cm^{-1}$), which were calculated from the measured optical densities of the solutions divided by the concentration of hydrated electrons generated by pulse radiation. The pattern of variation of the optical absorption spectra allows one to distinguish three consecutive steps preceding the formation of colloidal metal. The first step corresponds to the formation of the Pb^+ ion upon reduction of the Pb^{2+} ion by a hydrated electron. The Pb^+ ion is responsible for an absorption band with a maximum of 320 nm, which appears immediately after the pulse of accelerated electrons.[57-59] The second step, which lasts for ~30 μs, involves recombination of the Pb^+ ions giving a new species, which is characterized by a more intense optical absorption at $\lambda_{max} = 290$ nm. This species also accounts for the weak absorption band at 660 nm (it is not shown in Fig. 5). The product characterized by these optical absorption bands arises in a second-order reaction, which may be the formation of the Pb_2^{2+} dimer or the Pb^0 atom

$$Pb^+ + Pb^+ \longrightarrow Pb_2^{2+},$$

$$Pb_2^{2+} \rightleftharpoons Pb^0 + Pb^{2+}.$$
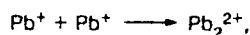
The third, fairly long, period is associated with the disappearance of the absorption bands attributed to Pb_2^{2+} or Pb^0 in a second-order reaction. This reaction is
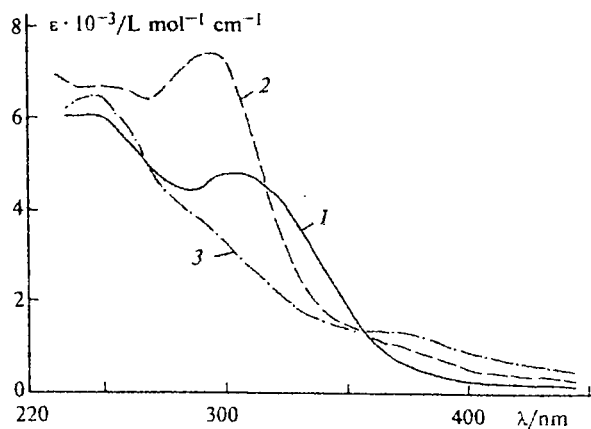

Fig. 5. Optical absorption spectra of lead clusters 1 μs (*1*), 30 μs (*2*), and 2 ms (*3*) after the action of a pulse of accelerated electrons on an aqueous solution containing $Pb(ClO_4)_2$ ($2\cdot10^{-2}$ mol L^{-1}) and Pr^iOH (0.1 mol L^{-1}). The irradiation gives $2.9\cdot10^{-6}$ mol L^{-1} of hydrated electrons.

completed after ~2.5 ms and yields a new lead cluster, which accounts for an optical absorption band with a maximum at 250 nm and a clear-cut shoulder at 370 nm. The assignment of this band to the Pb_4^{4+} cluster, having a square structure, conforms to the rule of the formation of intermediate clusters that we have proposed for silver. As metallic lead, Pb_4^{4+} has one electron per chemical bond. However, the high positive charge of this cluster might diminish its stability. Therefore, the possibility that recombination gives a cluster with a smaller positive charge, for example, Pb_3^{2+} or even Pb_2, rather than Pb_4^{4+} also cannot be ruled out. Unfortunately, we were unable to determine the nature of this cluster by pulse radiolysis or to detect more complex lead clusters. Subsequently the optical absorption, smoothly growing in the UV region, gradually increases. This process is completed over a period of several seconds and is due to the formation of colloidal silver. According to published data,[60,61] silver sols are characterized by an intense absorption band with $\lambda_{max} = 215$ nm ($\varepsilon = 3 \cdot 10^4$ L mol^{-1} cm^{-1}). Presumably, the larger lead clusters preceding the formation of colloidal particles absorb light in the same optical region and, therefore, their spectrum cannot be distinguished against the background of the spectrum of the colloidal particles themselves.

Table 2 presents characteristics of some short-lived metal clusters, whose formation was established and whose identification was sufficiently reliable. In essence, the examples are limited to metals in which the outer s- and p-orbitals are being filled. Detection of a palladium cluster formed upon radiation-induced reduction of palladium(II) in an aqueous solution in the presence of polyethyleneimine as a stabilizer has been reported.[62] This cluster is stable for several days and gradually transforms into colloidal metal. The spectrum of this

cluster exhibits an intense absorption band at 308 nm and a weaker band at about 400 nm. The cluster is readily oxidized with oxygen, H_2O_2, and methyl viologen and reacts with N_2O to give nitrogen. Its reaction with H_2S gives PdS and H_2. The proposed assignment of this species to the Pd_2^{2+} cluster seems hardly acceptable. More likely, it is a relatively large cluster comprising ~10 atoms. This is indicated by the data on the kinetics of its formation and subsequent transformation into colloidal metal, collected upon pulse irradiation of aqueous solutions of a palladium(II) salt.[63,64] It should be noted that pulse radiolysis study of clusters formed by metals with a vacant d-shell is hampered by the tendency of these metals to form intermediate relatively stable organometallic compounds. For example, the Ni^+ ion resulting from reduction of Ni^{2+} by hydrated electrons after pulse irradiation of aqueous solutions of nickel salts in the presence of organic compounds as scavengers of the ·OH radicals (alcohols) mostly disappears in reactions with organic radicals.[65] This gives rather stable organonickel compounds; their transformations also result ultimately in the formation of the colloidal metal. However, the nature of cluster species preceding this outcome remains unknown. The trend to form similar organometallic compounds has also been found for palladium[63,64] and platinum.[66]

Thus, the formation of short-lived clusters of various degrees of complexity proves to be a fairly common phenomenon for reduction of metal ions in aqueous solutions. They arise in the intermediate stages of the reduction and precede the formation of the colloidal metal. It was shown in relation to silver that this involves formation of "magic" clusters, *i.e.*, the clusters that are energetically and structurally most preferable.

Unfortunately, for most of metals, excluding silver, large clusters (consisting of more than four atoms),

Table 2. Formation pathways and optical characteristics of some clusters

Solution (concentrations/mol L^{-1})	pH	Reaction	$k \cdot 10^{-9}$ /L mol^{-1} s^{-1}	λ_{max} /nm	Reference
CuCl $(1 \cdot 10^{-4}-2 \cdot 10^{-3})$,	5.8	$Cu^0 + Cu^+ \longrightarrow Cu_2^+$	2.1	355	44
NaCl (2)		$2 Cu_2^+ \longrightarrow Cu_4^{2+}$	0.13	410	
Tl_2SO_4 $(2 \cdot 10^{-2})$,	6—13	$Tl^0 + Tl^+ \longrightarrow Tl_2^+$	1.4	245, 420, 700	40, 41, 43
		$2 Tl_2^+ \longrightarrow Tl_4^{2+}$		300	
InBr $(1 \cdot 10^{-3})$	6.8	$In^0 + In^+ \longrightarrow In_2^+$	1.5	460	45
		$2 In_2^+ \longrightarrow In_4^{2+}$	5.0	290	
$Hg_2(ClO_4)_2$ $(1 \cdot 10^{-4}-1.0)$	2.0	$Hg_2^{2+} + H \longrightarrow Hg_2^+$	4.5	285	56
		$Hg_2^+ + Hg_2^{2+} \longrightarrow Hg_4^{3+}$,	0.04	390	
		$Hg_4^{3+} \rightleftharpoons Hg_3^+ + Hg^{2+}$			
$Pb(ClO_4)_2$ $(2 \cdot 10^{-4})$, HCOONa (10^{-2})	5.4	$Pb^+ + Pb^+ \longrightarrow Pb_2^{2+}$ (or $Pb^0 + Pb^{2+}$)	8.2	290	59
		$2 Pb_2^{2+} \longrightarrow Pb_3^{2+} + Pb^{2+}$	2.2	250, 370	*

* The data of this work.

which are the direct precursors of sols, have not been detected experimentally. In all probability, this is due to the overlap of the optical bands of these clusters with the absorption of colloidal particles, formed in approximately the same time interval. Certainly, nucleation of other metals has common features with the nucleation of silver, considered here in detail. However, due to the problems faced by the studies of the intermediate stages of the process, no reliable mechanism for the formation of colloidal particles can be proposed for the majority of metals.

Until recently, the studies of positively charged metal clusters in aqueous solutions have been mostly limited to conditions under which they exist as simple cations. It can be expected that in the presence of certain ligands, they would react with them to give complexes. In fact, it has been found recently[67,68] that the silver atom and Ag_2^+ and, perhaps, Ag_3^{2+} cations form complexes with CN^-, EDTA, or NH_3. The optical properties, redox potentials, and kinetic characteristics of these clusters differ substantially from those for aquated clusters.

The silver nucleation in polymeric membranes,[69—71] in gelatin,[72] or on the surface of colloidal silicon[73] occurs by a similar mechanism, *i.e.*, it involves intermediate stages giving the same clusters as those formed in homogeneous aqueous solutions of silver ions, whose nature is described above in detail. Apparently, the main regularities of the reduction of silver ions in aqueous solutions are common to various systems. Therefore, it can be assumed that the initial steps of the photographic process also have much in common with the processes discovered for the radiation-induced reduction of silver in aqueous solutions. In particular, some of the "magic" silver clusters can apparently be associated with latent image centers.

Mixed metal clusters

Recently, the first experiments on the synthesis and study of short-lived mixed (heteronuclear) clusters of some metals were carried out using the pulse radiolysis method.[74—77] These species are formed when metal ions in unstable oxidation states, for example, Co^+, react with other metal ions in stable oxidation states, for example, with Ag^+. By using metal ions with various reduction potentials, conditions favorable for fast electron transfer or for the formation of mixed intermediate clusters were elucidated.

Figure 6 illustrates the process of formation of a short-lived mixed cluster in an argon-saturated aqueous solution containing $Co(ClO_4)_2$ ($2 \cdot 10^{-2}$ mol L^{-1}), $AgClO_4$ ($1 \cdot 10^{-4}$ mol L^{-1}), and isopropyl alcohol after a microsecond pulse of accelerated electrons.[74] The concentration of cobalt ions is much higher than that of silver ions; therefore, during the electron pulse, virtually all $\bar{e}_{aq}$ react with the cobalt ions
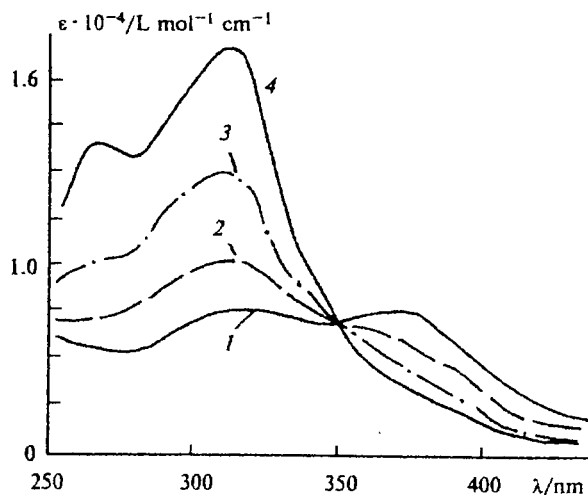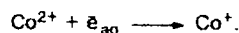

Fig. 6. Optical absorption spectra of mixed clusters 0.4 (*1*), 2 (*2*), 6 (*3*), and 25 μs (*4*) after the action of a pulse of accelerated electrons on an aqueous solution containing $Co(ClO_4)_2$ ($2.5 \cdot 10^{-2}$ mol L^{-1}), $AgClO_4$ ($1 \cdot 10^{-4}$ mol L^{-1}), and PrⁱOH (0.1 mol L^{-1}). The irradiation gives $9 \cdot 10^{-7}$ mol L^{-1} of hydrated electrons.

$$Co^{2+} + \bar{e}_{aq} \longrightarrow Co^+.$$

Within 0.4 μs after the pulse, optical absorption bands at 310 and 370 nm, due to the Co^+ ion, are observed in the spectrum.[78] In the absence of silver ions, the decay of this absorption is described by a second-order equation and is a result of interaction of the Co^+ ions with alcohol radicals. In the presence of silver ions, absorption of the Co^+ ions disappears much faster and follows the pseudo-first-order kinetics. The reaction rate constant is proportional to the concentration of the
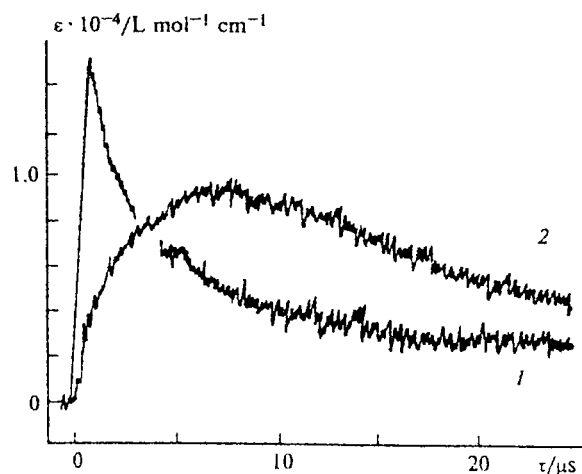

Fig. 7. Kinetic curves at λ = 430 (*1*) and 550 nm (*2*). For the solution composition and irradiation conditions, see Fig. 6.

silver ions present. It follows from Fig. 6 that the reactions with silver ions lead to the formation of absorption in the UV region (at wavelengths of less than 350 nm) and after 25 μs, a clear and typical absorption spectrum of the Ag_3^{2+} cluster, consisting of two bands with maxima at 310 and 265 nm, can be observed. Optical changes occur also in the visible region in which neither Co^+ nor the products formed at early stages of reduction of silver ions absorb. Figure 7 shows the building up of the absorption at 550 nm. The rates of the building up of the absorption are proportional to the concentration of silver ions. The absorption band of the Co^+ ions at 430 nm (it is also shown in Fig. 7) disappears at the same rates at which the absorption at 550 nm increases. The latter band can be attributed to the mixed $(CoAg)^{2+}$ cluster, which arises in the reaction

$$Co^+ + Ag^+ \longrightarrow (CoAg)^{2+}.$$

After ~6 μs, the absorption at 550 nm starts to diminish; the rates of its decay are also proportional to the concentration of the silver ions. As a consequence, 25 μs later, Ag_3^{2+} clusters are formed in the following reactions:

$$(CoAg)^{2+} + Ag^+ \longrightarrow Co^{2+} + Ag_2^+,$$

$$Ag_2^+ + Ag^+ \longrightarrow Ag_3^{2+}.$$
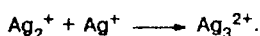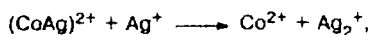
When the times are longer, the process develops by a mechanism typical of solutions containing only silver ions, i.e., more complex clusters, Ag_4^{2+} and Ag_8^{2+}, are formed and subsequently colloidal silver appears.

The absorption spectrum of the mixed cluster $(CoAg)^{2+}$ (Fig. 8) was obtained by a computer simulation for various wavelengths taking account of the known

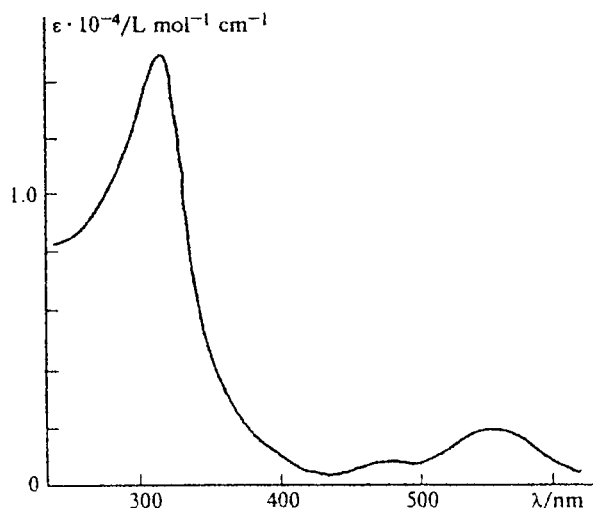Fig. 8. Optical absorption spectrum of the $(CoAg)^{2+}$ cluster.

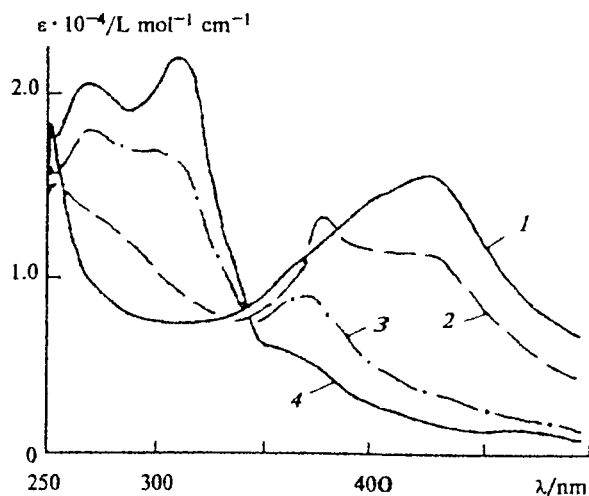Fig. 9. Optical absorption spectra of mixed clusters 0.3 (*1*), 1.9 (*2*), 8.8 (*3*), and 25 μs (*4*) after the action of a pulse of accelerated electrons on an aqueous solution containing Tl_2SO_4 $(1 \cdot 10^{-2}$ mol $L^{-1})$, $AgClO_4$ $(1 \cdot 10^{-4}$ mol $L^{-1})$, and Pr^iOH (0.1 mol L^{-1}). The irradiation gives $5.5 \cdot 10^{-7}$ mol L^{-1} of hydrated electrons.

rate constants for the formation and decay of the Co^+ ions and silver clusters, and also the corresponding extinction coefficients. It can be seen that this cluster is responsible for an intense absorption band at 310 nm and a substantially weaker band at 550 nm.

Similar experimental approaches were used to prepare other mixed clusters,[74,75] $(CdAg)^{2+}$, $(CdTl)^{2+}$, and $(TlAg)^+$. Figure 9 illustrates the formation of $(TlAg)^+$ in a solution containing Tl_2SO_4, $AgClO_4$, and isopropyl alcohol.[75] Within 0.3 μs after the electron pulse, the absorption spectrum of Tl_2^+ is observed as a broad band with a maximum at 420 nm.[40—43] The decay of Tl_2^+ is accompanied by the appearance of a new band at 370 nm. In turn, the disappearance of the latter band is accompanied by the formation of typical absorption bands of the Ag_3^{2+} cluster. The band at 370 nm is due to the mixed cluster $(TlAg)^+$, which is produced by the following scheme:

$$Tl_2^+ + Ag^+ \longrightarrow (TlAg)^+ + Tl^+.$$

The equilibrium constant of the reaction

$$Tl^0 + Tl^+ \longrightarrow Tl_2^+$$
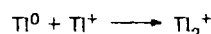
ranges from $2.3 \cdot 10^3$ to $1.4 \cdot 10^2$ mol L^{-1}.[41,43] This means that the enthalpy of formation of Tl_2^+ is very low; it is only -0.17 or -0.13 eV. Therefore, this complex might also arise by the reaction
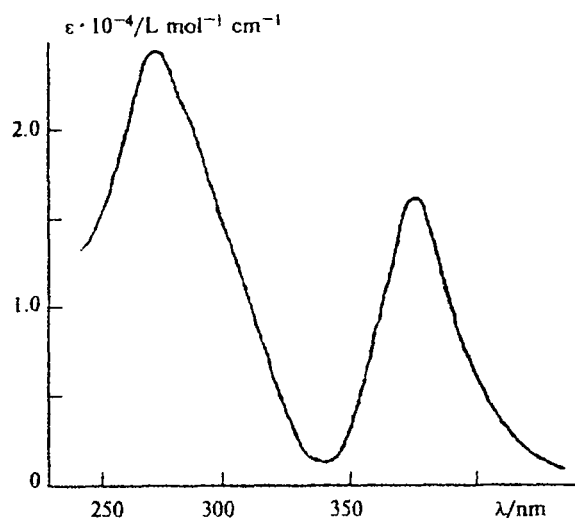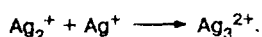
$$Tl^0 + Ag^+ \longrightarrow (TlAg)^+.$$
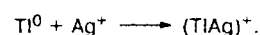
Fig. 10. Optical absorption spectrum of the $(TlAg)^+$ cluster.

Simple silver clusters are formed in reactions of mixed clusters with silver ions

$$(TlAg)^+ + Ag^+ \longrightarrow Ag_2^+ + Tl^+,$$

$$Ag_2^+ + Ag^+ \longrightarrow Ag_3^{2+}.$$

The absorption spectrum of the mixed cluster $(TlAg)^+$ contains two intense bands at 375 and 270 nm (Fig. 10).

It was shown that unlike Cd^+ ions, the Zn^+ ions formed upon the reduction of the Zn^{2+} ion by hydrated electrons react with silver, thallium, and cadmium ions with electron transfer giving no mixed clusters.[74,76,77]

Figure 11 illustrates this process for a solution, containing $ZnSO_4$, Tl_2SO_4, and isopropyl alcohol.[75] Immediately after the electron pulse, the spectrum contains an absorption band at 310 nm, which corresponds to the Zn^+ ion. In the presence of thallium ions, the disappearance of this band substantially accelerates and follows pseudo-first-order kinetics. As the Zn^+ ions disappear, absorption of Tl^0 atoms appears (a broad low-intensity band at 460 nm). Figure 12 shows the kinetics of their formation followed by their decay over longer periods of time. The Zn^+ ions reduce the Tl^+ ions in the electron transfer reaction

$$Zn^+ + Tl^+ \longrightarrow Zn^{2+} + Tl^0$$

to give thallium atoms. The formation of the latter, instead of the Tl_2^+ ions, is due to the fact that at the given concentration of the Tl^+ ions, the equilibrium of the formation of Tl_2^+ is shifted toward free thallium atoms.

It has been shown[75] that the Tl_2^+ ion reduces a Pb^{2+} ion in an electron transfer reaction; this affords a lead ion in an unusual oxidation state, Pb^+:

$$Tl_2^+ + Pb^{2+} \longrightarrow 2\ Tl^+ + Pb^+.$$
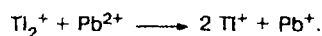
The redox potentials of the metal ions in unusual oxidation states, whose reactions are studied in this work, are known.[3,4] They are presented below.

Pair	E^0/V	Pair	E^0/V
Ag^+/Ag^0	-1.8	$Tl_2^+/2Tl^+$	-1.8
Cd^{2+}/Cd^+	-1.9	Zn^{2+}/Zn^+	-2.5
Tl^+/Tl^0	-1.9	Pb^{2+}/Pb^+	-1.0

Table 3 contains the characteristics of the studied reactions of metal ions in unusual oxidation states. It can be seen that mixed clusters are formed in those cases
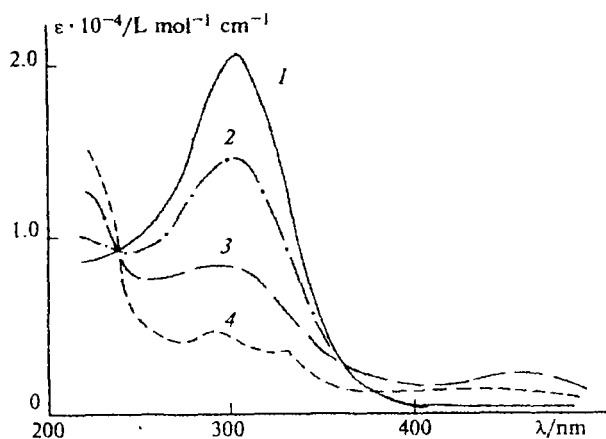

Fig. 11. Optical absorption spectra 0.6 (1), 9.2 (2), 26 (3), and 62 μs (4) after the action of a pulse of accelerated electrons on an aqueous solution containing $ZnSO_4$ ($4 \cdot 10^{-2}$ mol L^{-1}), Tl_2SO_4 ($1 \cdot 10^{-4}$ mol L^{-1}), and Pr^iOH (0.1 mol L^{-1}). The irradiation gives $5.3 \cdot 10^{-6}$ mol L^{-1} of hydrated electrons.
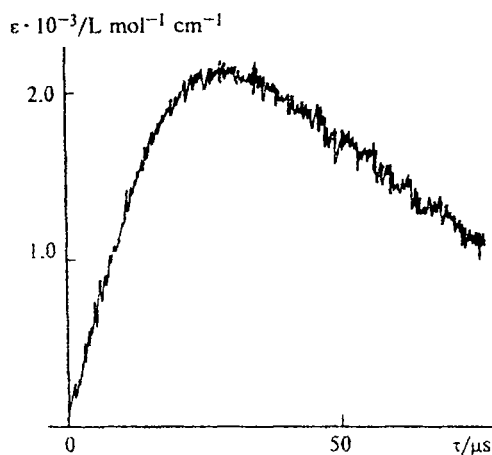

Fig. 12. Kinetic curve at $\lambda = 460$ nm. For the solution composition and irradiation conditions, see Fig. 11.

Table 3. Characteristics of the reactions of metal ions in unusual oxidation states

| Reaction	$\Delta E = E_1^0 - E_2^0/V$	Type of electron interaction	λ_{max}/nm (cluster)
$Co^+ + Ag^+ \longrightarrow (CoAg)^{2+}$	0	$4s^1 + 5s^0 \longrightarrow \sigma_s$	310, 550
$Cd^+ + Ag^+ \longrightarrow (CdAg)^{2+}$	−0.1	$5s^1 + 5s^0 \longrightarrow \sigma_s$	270, 330
$Tl_2^+ + Ag^+ \longrightarrow (TlAg)^+ + Tl^+$	0	$6p^1 + 5s^0 \longrightarrow \sigma_{sp}$	270, 335
$Tl_2^+ + Cd^{2+} \longrightarrow (TlCd)^{2+} + Tl^+$	−0.1	$6p^1 + 5s^0 \longrightarrow \sigma_{sp}$	~300
$Zn^+ + Ag^+ \longrightarrow Zn^{2+} + Ag^0$	−0.7	Electron transfer	
$Zn^+ + Tl^+ \longrightarrow Zn^{2+} + Tl^0$	−0.6	The same	
$Tl_2^+ + Pb^{2+} \longrightarrow 2\,Tl^+ + Pb^+$	−0.8	»	

where the electrochemical potentials of the reacting ions are equal or sufficiently close. In addition, a necessary condition is the possibility of the formation of a bonding molecular orbital from the atomic orbitals of the reacting metal ions. In fact, the standard reduction potentials of silver, cadmium, and thallium pairs coincide to within the accuracy of their measurement. Bonding molecular orbitals σ_s or σ_{sp} can also be formed from the s- or p-orbitals of the reacting ions. Therefore, mixed clusters actually do form. In the case of cobalt, the potential is unknown. The fact that the mixed $(CoAg)^{2+}$ cluster forms makes it possible to conclude that the potential of the Co^{2+}/Co^+ pair is close to −1.8 V. The Co^+ ion has one electron in the outer s orbital; this electron can interact with the 5s-orbital of the silver ion giving a bonding σ_s molecular orbital in the mixed $(CoAg)^{2+}$ cluster. Apart from the above-considered cases where short-lived mixed clusters are formed, reactions involving the Ni^+ ion were also studied. However, neither formation of mixed clusters with other metal ions nor even reactions with fast electron transfer were observed in this case. This result can be explained taking into account the d-electron configuration of this ion, which does not favor the formation of a bonding molecular orbital with s- or p-orbitals of the metal ions studied. The low reactivity of this ion toward the electron transfer had also been explained earlier by its d-electron configuration.[79] It is of interest that although the Ni^+ ions, arising in the initial stage of reduction of the Ni^{2+} ions (a solution of $Ni(ClO_4)_2$ $(2 \cdot 10^{-2}$ mol $L^{-1})$, $AgClO_4$ $(1 \cdot 10^{-4}$ mol $L^{-1})$, and isopropyl alcohol $(0.1$ mol $L^{-1}))$ by hydrated electrons, do not react with silver ions to give a mixed cluster, colloidal silver proves to be the final reduction product. It is formed about 0.4 s after the action of the electron pulse.[74] Apparently, this is a result of interaction of silver ions with a long-lived organometallic complex comprising an Ni^+ ion and a $Me_2C \cdot OH$ radical.[65] The fast electron transfer in reactions between metal ions occurs in those cases where their standard redox potentials differ markedly. This situation is realized for some of the metal ions studied (see Table 3).

In connection with the problem of the intermediate formation of mixed short-lived clusters during the reduction of metal ions in aqueous solutions discussed

here, the publication[80] that largely stimulated these studies should be mentioned. In this work, it was found that during pulse irradiation of an aqueous solution of $Pb(ClO_4)_2$ $(1 \cdot 10^{-2}$ mol $L^{-1})$, $AgClO_4$ $((2.5$ to $20.0) \cdot 10^{-5}$ mol $L^{-1})$, and $HCOONa$ $(1 \cdot 10^{-2}$ mol $L^{-1})$, virtually all the $CO_2^{\cdot-}$ radical anions formed under these conditions reduce the Pb^{2+} ions in the initial stage. In the opinion of the authors cited,[80] the Pb^+ ions thus formed are subsequently transformed upon disproportionation into the Pb^0 atoms. The decay of the latter yields a species, which can be unambiguously identified as the Ag_4^{2+} cluster based on its optical characteristics. It was suggested that Pb^0 reacts with Ag^+ ions to give the $PbAg^+$ complex, which is then transformed into Ag_4^{2+} as a result of successive reactions with silver ions. Moreover, a very weak absorption band (virtually two orders of magnitude weaker than those due to other species arising under these conditions) with a maximum at 460 nm was detected in the spectrum. According to the published data,[80] the disappearance of this absorption correlated with the appearance of the absorption of the Ag_4^{2+} cluster. However, in our opinion, there are no grounds to expect the formation of a mixed cluster of the $PbAg^+$ type in this case because the Pb^{2+}/Pb^0 $(-1.0$ V) and Ag^+/Ag^0 $(-1.8$ V) potentials are substantially different. In fact, it follows from the above discussion that for mixed clusters to be formed, it is necessary that the redox potentials of the components be close. It is more likely that this process involves the Pb_2^{2+} cluster, which can occur in equilibrium with lead atoms in aqueous solutions of lead ions, as was found for thallium. The subsequent disappearance of the Pb_2^{2+} ions can be due to the formation of the Ag_4^{2+} cluster. This cluster is also formed in a pseudo-first-order reaction with respect to the silver ions; the measured rate constant is $8 \cdot 10^7$ L mol^{-1} s^{-1}. In our opinion, the observed changes in optical absorption should be attributed to the first stage, *i.e.*, to the formation of an intermediate mixed cluster that absorbs at 460 nm according to the following reactions:

$$Pb_2^{2+} + Ag^+ \longrightarrow (Pb_2Ag)^{3+},$$

$$(Pb_2Ag)^{3+} + Ag^+ \longrightarrow (Pb_2Ag_2)^{4+}.$$
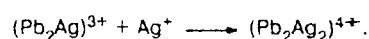
The addition of the first silver ion is the rate-determining step of this reaction. In the second stage, the mixed cluster is transformed into a simple silver cluster

$$(Pb_2Ag_2)^{4+} + Ag^+ \longrightarrow 2\,Pb^{2+} + Ag_3^+,$$

$$Ag_3^+ + Ag^+ \longrightarrow Ag_4^{2+}.$$
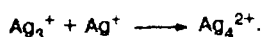
The rates of the second stage are also limited by the first reaction. This approach eliminates the contradiction concerning the relationship between the reduction potentials of the components forming the mixed cluster of lead and silver, which appears when this species is identified as $(PbAg)^+$, as was done in the study discussed above.[80] In fact, in the case of the $(Pb_2Ag_2)^{4+}$ species, it can be expected that the similarity of the potentials of the components, which is required for the formation of a mixed cluster, would be fulfilled. The $E^0(2Pb^{2+}/Pb_2^{2+})$ value should be smaller than $E^0(Pb^{2+}/Pb^0)$ by the energy of complexation of the Pb^0 atom by the Pb^{2+} ion, i.e., it is only slightly smaller than -1.0 V, which is very close to $E^0(2Ag^+/Ag_2) = -0.97$ V.[14]

The results considered above demonstrate that the formation of mixed metal clusters is most efficient when silver ion is one of the components. Apparently, silver ions possess an especially high capability of binding metal ions in unusual oxidation states carrying an unpaired electron in an outer s- or p-orbital. It can be suggested that other short-lived mixed metal clusters would also be discovered in the future. The conditions of their formation have been formulated in this work and can serve as a guide for the targeted search for these species.

* * *

The cluster chemistry, which is being vigorously developed, mostly involve preparative synthesis of stable cluster compounds of transition metals; primary attention is concentrated on the characteristic features of the interaction of metals with one another and with the ligands surrounding them and on the structure of cluster molecules.[24,25] A close packing of ligands on the cluster surface is apparently a necessary condition that ensures the cluster stability. The ligand shell decreases the surface energy and creates steric hindrance hampering coalescence of the metal aggregates. "Naked" clusters are extremely unstable, and special expedients for their stabilization on cooled surfaces or in inert matrices are needed (see, for example, Ref. 81). We have every reason to believe that small clusters comprising from 2 to 10 atoms are formed in intermediate stages of various chemical processes related to metal oxidation or reduction. They play an important role in catalysis, electrochemistry, and other fields of chemistry.

The experimental data considered in this review were obtained using pulse radiolysis. As a result, the nature and the role of clusters in a particular radiation-induced

chemical reduction of metal ions in aqueous solutions were established. However, in our opinion, the significance of radiation-chemical studies carried out here is much wider. They model to a degree the general mechanism of the chemical reduction of metal ions and illustrate the sequence and diversity of small clusters preceding the evolution of the metal phase. In particular, certain types of silver clusters discovered here can be associated with those species that arise as latent image centers in photography. The generally accepted point of view is that there exists some critical size of a silver aggregate possessing the catalytic properties needed for the development of the photographic process.[82] Although the mechanism of the catalytic action remains obscure, it might be due to the ability of these aggregates to add sequentially an additional number of silver ions, i.e., to acquire a positive charge. For example, it is assumed[83,84] that the Ag_3 cluster contacting with AgBr is transformed into the tetrahedral Ag_4^+ cluster. A cluster with the same composition has been detected by optical spectroscopy and ESR in 0.1 M water—alcohol solutions of $AgClO_4$ exposed to γ-radiation at the liquid-nitrogen temperature.[38] A fundamental feature that distinguishes the reductive aggregation of silver in aqueous solutions at room temperature from that in frozen solutions is the possibility of diffusion of silver clusters and their coalescence upon collisions in the solution bulk. The metal nucleation results from sequential coalescence of silver clusters. Thus, coalescence of the Ag_4^{2+} clusters affords a more complex cluster, Ag_8^{2+}, which, in turn, is a precursor of larger clusters and, subsequently, metal sols. At low temperatures in frozen water—alcohol solutions of $AgClO_4$, the mobility of large clusters is limited due to the high viscosity, and conditions of a photographic process are realized to some extent. The growth of silver aggregates is mainly due to the reduction of the silver ions, attached to the cluster (sorbed), by more mobile organic radicals and reducing molecules. The silver atoms in frozen water—alcohol solutions aggregate *via* successive steps giving Ag_2^+ and Ag_3^{2+}, and finally Ag_4^{2+}. Apparently, this cluster acts as the center of the subsequent growth of the metal nuclei. It is reduced by alcohol radicals to Ag_4^+, which is followed by gradual silver nucleation to give colloidal metal.

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