Russian Chemical Reviews **66** (2) 93 – 105 (1997) © 1997 Russian Academy of Sciences and Turpion Ltd

UDC 541.5:541.15:541.65:530.145.539.184

Metal ions in unusual and unstable oxidation states in aqueous solutions: preparation and properties

B G Ershov

Contents

I.	Introduction	93
II.	Radiation-chemical preparation of atoms and ions of metals in unusual oxidation states	93
III.	Atoms and ions of metals in unusual oxidation states in aqueous solutions	94
IV.	Atoms and ions of metals in unusual oxidation states in frozen aqueous solutions	97
V.	Regularities in the variation of electronic properties	98
VI.	Oxidation-reduction potentials	101
VII.	Regularities in the variation of the dissociation constants of complexes	103
VIII.	Conclusion	103

Abstract. The properties of short-lived metal atoms and ions in unusual oxidation states in aqueous solutions, characterised by the presence of one electron in the outer *s* or *p* orbitals (the $d^{10}s^1$ and $d^{10}s^2p^1$ configurations respectively), are discussed. The results of studies on such ions by pulse radiolysis with rapid optical detection and by the matrix isolation method in frozen aqueous solutions are presented. The nature of the dependences of funda mental characteristics of metal atoms and ions (optical transition energies, the electronic structures of various complexes, the oxidation-reduction potentials, *etc.*) on their positions in the Periodic System are analysed. The bibliography includes 93 references.

I. Introduction

Atoms and ions in unusual and unstable oxidation states are formed at intermediate stages of oxidation-reduction reactions occurring with participation of polyvalent metals. Despite the short time of their existence, their important role in the occurrence and effectiveness of many processes in chemistry and biology is evident. The existence of metal ions in unusual oxidation states has been postulated, and in a number of instances has been confirmed experimentally, in connection with the justification of the multistage nature of electrochemical reactions and the explanation of catalytic steps with participation of metals and the characteristic features of the mechanisms of many other oxidation-reduction processes. The above species can be obtained by pulse radiolysis in aqueous solutions in one-electron reduction or oxidation reactions of metal ions and they are investigated with the aid of optical or coulometric detection. Procedures involving the radiation-induced generation of metal ions in unusual oxidation states in inert matrices at a low temperature with subsequent study by stationary optical and EPR spectroscopic methods are also widely employed.

B G Ershov. Institute of Physical Chemistry, Russian Academy of Sciences, Leninskii prosp. 31, 117915 Moscow, Russian Federation. Fax (7-095) 335 17 78. Tel. (7-095) 128 79 34

Received 5 July 1996
Uspekhi Khimii **66** (2) 103 – 116 (1997); translated by A K Grzybowski

During the last thirty years investigators have studied in fair detail, employing the above approaches, the properties of many metal ions in unusual valence forms in aqueous media. The results of studies available by 1981 were analysed in our previous review.[1] New data, which make it possible to reach definite conclusions about the regularities in the variation of fundamental properties of metals in unusual oxidation states as a function of their position in the Periodic System, have now accumulated. The study of the chemistry of such elements has become possible as a result of advances, in the first place in radiation chemistry, and also the development of the method of pulse radiolysis.[2]

This review is devoted to a discussion of the properties of metals in unusual and unstable oxidation states in aqueous solutions and to the establishment of the regularities in their manifestation as a function of the position of the element in the Periodic System. The review is concerned predominantly with metal ions having one electron in the outer *s* and *p* orbitals, *i.e.* with the $d^{10}s^1$ and $d^{10}s^2p^1$ electronic configurations (copper, silver, gold, zinc, cadmium, mercury, gallium, indium, thallium, tin, lead, antimony, and bismuth).

II. Radiation-chemical preparation of atoms and ions of metals in unusual oxidation states

The radiation-chemical reduction or oxidation of metal ions in aqueous solutions is effected by the ionic and radical species which arise on decomposition of water as a result of its interaction with ionising radiation. In a general form, the latter process can be described by the following equation:

$$H_2O \rightsquigarrow e^-_{aq}\ (2.7),\ H\ (0.5),\ OH\ (2.9),\ H_2\ (0.5),\ H_2O_2\ (0.7),\ H^+\ (2.7).$$

The primary radiation-chemical yields of the species in the solution volume per 100 eV of the absorbed energy for light types of radiation (γ-rays or accelerated electrons), the linear energy transfer for which is small, are presented in brackets. The hydrated electron e^-_{aq} and the hydrogen atom H formed have high reduction potentials (−2.7 and −2.3 V respectively), while the hydroxyl radical OH has a high oxidising capacity (2.9 V). For this reason, when the ratio of the potentials in their interaction with metal ions satisfies the requirement that the free energy of the system diminishes, one-electron reduction or oxidation reactions take place. For example, both processes take place in the case of Pb^{2+} ions.

$$Pb^{2+} + e^-_{aq} \rightarrow Pb^+,$$

$$Pb^{2+} + OH \rightarrow Pb^{3+} + OH^-.$$

Under these conditions, ions in unusual and unstable oxidation states are produced. They have the electronic configurations $d^{10}s^1$ and $d^{10}s^2p^1$ for Pb^{3+} and Pb^+ respectively.

As a rule investigators used for the study of metal ions in unusual oxidation states solutions in which predominantly reducing or oxidising species may be obtained. We shall illustrate this in relation to OH radicals. On order to obtain OH radicals, a solution is saturated with nitrous oxide. The limiting concentration of the gas under normal conditions in a neutral solution is ~ 0.05 M. As a result of the reaction

$$N_2O + e^-_{aq} + H_2O \rightarrow N_2 + OH + OH^-,$$

the rate constant for which is 9×10^9 litre mol^{-1} s^{-1},[3] virtually only hydroxyl radicals are formed in aqueous solution.

Hydrated electrons alone may be obtained only in alkaline solutions (pH > 12), saturated with molecular hydrogen, via the following reactions:

$$H_2 + OH \rightleftarrows H + H_2O,$$

$$H + OH^- \rightleftarrows e^-_{aq} + H_2O.$$

The pK for the second equilibrium is 9.6, *i.e.* the hydrogen atom is a weak acid. However, the rate constant for the reaction of molecular hydrogen with the hydroxyl radical is insufficiently high (3.7×10^7 litre mol^{-1} s^{-1}). In order to increase the rate of reaction, it is necessary to employ high hydrogen pressures, which is difficult to achieve experimentally. Furthermore, hydrogen atoms are transformed into hydrated electrons only in a highly alkaline medium, where many metal ions are precipitated in the form of hydroxides. Therefore, in order to create a reducing medium, use is made of aqueous solutions to which organic compounds — alcohols or organic acid salts — are added as hydroxyl radical and hydrogen atom scavengers. For example, when isopropyl alcohol or a formic acid salt is added, the reactions

$$(CH_3)_2CHOH + OH\,(H) \rightarrow (CH_3)_2COH + H_2O\,(H_2),$$

$$HCOO^- + OH\,(H) \rightarrow COO^- + H_2O\,(H_2),$$

generate only reducing species — hydrated electrons and organic radicals — on exposure to ionising radiation. The oxidation-reduction potentials (E^0) of certain organic radicals, most frequently employed in radiation-chemical studies, have been determined from measured equilibrium constants for the reactions involving the reduction of thallium ions by such radicals ($E^0 = -1.94$ V). The following values were obtained:[4,5]

Parameter	CO_2^-	$(CH_3)_2COH$	CH_3CHOH	CH_2OH
$-E^0$/V	1.9	1.39	1.25	1.18

The presence of one electron in the outer *s* or *p* orbital of the metal atom or ion is responsible for an exceptionally high reactivity. Such species may be compared with radicals, which also have an unpaired electron. The lifetimes of metal ions belonging to the *s* and *p* blocks and having unusual oxidation states in aqueous solutions are determined by kinetic factors. The rate constants for their dimerisation or disproportionation are as a rule $10^9 - 10^{10}$ litre mol^{-1} s^{-1}. The preparation and study of such species in aqueous solutions are therefore associated with the employment of methods which make it possible to detect fast processes, in the first place pulse radiolysis with optical detection of short-lived products,[1,2,6] as well as low-temperature radiolysis [usually in glassy aqueous solutions at the temperature of liquid nitrogen (77 K)]. The method involving the matrix isolation of the highly reactive species formed under these conditions makes it possible to investigate them by stationary electron spin resonance (ESR) or optical spectroscopic methods.

III. Atoms and ions of metals in unusual oxidation states in aqueous solutions

1. Copper, silver, and gold atoms

The radiation-chemical reduction of silver has been most thoroughly investigated.[7–9] We shall deal in somewhat greater detail with the methodological features of the experiments on the preparation and study of silver atoms in aqueous solutions, because they are fairly applicable also to other metals.

In a dilute aqueous solution of a silver salt ($AgClO_4$ at a concentration of $10^{-5} - 10^{-3}$ M is usually employed), containing alcohol or HCOONa as the hydroxyl radical scavenger, an intense optical absorption due to the hydrated electron with $\lambda_{max} = 720$ nm is observed immediately after the application of a short electron pulse (with a nano- or micro-second duration). The decrease in this absorption is accompanied by the appearance of a new absorption band with $\lambda = 360$ nm. The rates of decrease in the intensity of the first absorption and of increase in that of the second are proportional to the concentration of the silver ions present in the solution. When the solutions are saturated with nitrous oxide, the hydrated electrons are transformed into OH radicals. The appearance of a band with $\lambda = 360$ nm is not then observed. The observed changes in the optical absorption spectra are probably caused by the reaction

$$Ag^+ + e^-_{aq} \rightarrow Ag.$$

This hypothesis has been confirmed by the observation of the effect of ionic strength on the rate of reaction which is of the kind expected for the interaction of species bearing unlike charges. The conductivity of the aqueous solution increases under these conditions owing to the formation of a proton.

The rate constant for the reduction of silver ions by electrons has been determined from the analysis of the kinetics of the decrease in the optical absorption due to the hydrated electron, which is described by pseudo-first-order kinetics. The rate constant was found to be 4.8×10^{10} litre mol^{-1} s^{-1}.[9] In the measurement of the optical spectrum of atomic silver, it is essential to bear in mind that its absorption bands overlap with those of the hydrated electron and the organic radical, formed immediately after the application of the accelerated electron pulse and disappearing in subsequent reactions, and also with the bands due to a new species — the Ag_2^+ cluster generated in the reaction

$$Ag + Ag^+ \rightarrow Ag_2^+.$$

Bearing this in mind, Ershov *et al.*[9] exposed a deaerated $AgClO_4$ solution (1×10^{-4} M) containing 0.1 M isopropyl alcohol to a short 15 ns electron pulse, the absorption spectrum being measured after 0.1 μs. During the time elapsed, only 36% of the hydrated electrons were trapped by the silver ions. Allowance for the absorption due to the remaining hydrated electrons and $(CH_3)_2COH$ radicals, as well as the silver ions consumed as a result of the reduction made it possible to calculate the absorption spectrum due to Ag^0 atoms in the aqueous solution. The spectrum consists of a broad band with $\lambda = 360$ nm; the extinction coefficient (ε) is 1.6×10^4 mol litre cm^{-1}, whilst the band width at the half the height is 0.91 eV (Fig. 1).

The preparation of copper atoms in unusual oxidation states is complicated compared with the preparation of silver atoms by the fact that in aqueous solutions copper in the stable state has a degree of oxidation of +2. Solutions of copper salts in the +1 oxidation state are unstable and are readily oxidised to the +2 state. In order to increase their stability, ligands capable of forming copper(I) complexes are added to the solution. Sukhov *et al.*[10] used neutral aqueous deaerated CuCl solutions ($1 \times 10^{-4} - 3 \times 10^{-3}$ M) containing 2 M NaCl. Under these conditions, copper(I) ions exist predominantly as the complexes $CuCl_3^{2-}$ (80%) and $CuCl_2^-$ (20%). It was observed that, after irradiation with accelerated electrons for 15 ns, the decrease in the absorption due to hydrated electrons at 720 nm is accompanied by the appearance of an absorption band with $\lambda = 380$ nm.

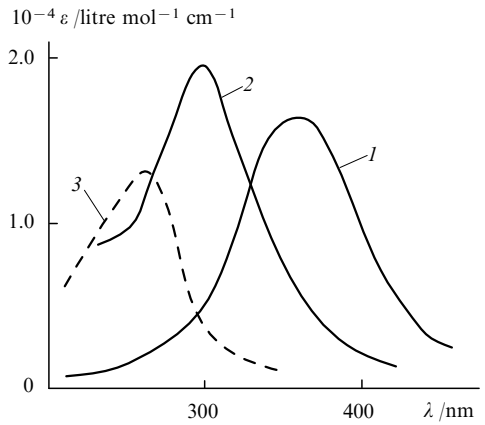


Figure 1. Optical absorption spectra of the atoms and ions of metals with the $d^{10}s^2p^1$ electronic configuration in water.
(*1*) Ag^0; (*2*) Cd^+; (*3*) In^{2+}.

However, in contrast to the analogous processes described above for silver ions, the increase in the intensity of the band with $\lambda = 380$ nm is slower than the decrease in the intensity characterising the disappearance of hydrated electrons. Furthermore, the rate of destruction of the latter was proportional to the concentration of the copper(I) ions present in the solution. However, this did not affect the appearance of the new band. The kinetics of the disappearance of e_{aq}^- in CuCl solutions are described satisfactorily by a first-order equation with an effective rate constant which depends linearly on the concentration of the dissolved salt. All these features suggest that the electrons are destroyed in a reaction of the type

$$CuCl_3^{2-} + e_{aq}^- \rightarrow CuCl_3^{3-}.$$

The calculated effective rate constant for the interaction of e_{aq}^- with monovalent copper(I) chloride complexes is 2.7×10^{10} litre mol^{-1} s^{-1}.[10] We may note that the hydroxyl radicals formed oxidised copper(I) to copper(II). Analysis of the characteristic features of the kinetics of the appearance of the absorption band with $\lambda = 380$ nm suggests that it is due to the copper atoms formed in the decomposition of the unstable chloride complex:

$$CuCl_3^{3-} \rightarrow Cu^0 + 3Cl^-.$$

The kinetics of the formation of copper atoms are described by a first-order equation with an effective rate constant of 4.7×10^7 s^{-1}.[10]

About thirty years ago, it was established[11] that the product of the reduction of the $Au(CN)_2^-$ ion by hydrogen atoms in an aqueous acid solution has an absorption band with a maximum at 260 nm, while the product of the reduction by hydrated electrons in a neutral medium is characterised by a band with a maximum at 410 nm. It has been suggested that the above absorption bands are associated with the adducts $HAu(CN)_2^-$ and $[Au(CN)_2^- ... e_{aq}^-]$. In a later publication,[12] it was shown that reduction with formation of a product in three equilibrium forms depending on the pH, each of which is characterised by different optical absorption bands, does indeed take place in both cases.

$$\underset{410\text{ nm}}{Au(CN)_2^{2-}} + 2H^+ \rightleftarrows \underset{430\text{ nm}}{HAu(CN)_2^-} + H^+ \rightleftarrows \underset{260\text{ nm}}{H_2Au(CN)_2}.$$

The pK is 5.9 and $\sim$5.2 for the first and second equilibria respectively. It was also established that all three complexes decompose with formation of gold atoms, which have a low-intensity absorption band with $\lambda_{max} < 260$ nm. The reaction is first-order with rate constants of 6.7×10^3 and 5.3×10^4 s^{-1} for $Au(CN)_2^{2-}$ and $H_2Au(CN)_2$ respectively.

2. Zn^+, Cd^+, and Hg^+ ions

The formation of monovalent zinc and cadmium ions as a result of reduction by hydrated electrons of the divalent metal ions in neutral aqueous solutions was observed more than twenty years ago.[13–15] It was found that the univalent ions have intense absorption bands at 300 nm. The results of the latest more careful experiments[16] suggest that the Zn^+ ion does indeed have an absorption band with a maximum at 310 nm, while the absorption band due to the Cd^+ ion is probably at 295 nm (Fig. 1). The formation of Hg^+ ions was observed in the reduction of divalent mercury by hydrogen atoms in aqueous media.[17,18] A feature distinguishing this species from those examined above with the $d^{10}s^1$ electronic configuration is the presence of two absorption bands with maxima at 225 and 255 nm,[17] which is apparently a consequence of the splitting of the p level. The Hg^+ ion hydrolyses in solution:

$$Hg^+ + H_2O \rightleftarrows HgOH + H^+.$$

The logarithm of the equilibrium constant of this reaction is 5.1.[18] According to the study quoted, the hydroxo-complex HgOH is characterised by two absorption bands — at 233 and 265 nm. The presence of an additional band with a maximum at 360 nm has also been established.[19] We may note an interesting feature of the formation of the Hg_2^{2+} ion by the dimerisation of Hg^+ ions. The process is complex and takes place in two consecutive reactions: in the first, the disproportionation of Hg^+ ions results in the formation of a mercury atom, while in the second the atom reacts with a Hg^{2+} ion, affording Hg_2^{2+}.

It has been shown[20] that $HgCl_2$ molecules interact with hydrated electrons:

$$HgCl_2 + e_{aq}^- \rightarrow HgCl + Cl.$$

The rate constant for this reaction (2.7×10^{10} litre mol^{-1} s^{-1}) is high.

The HgCl molecules are characterised by two optical absorption bands — at 245 and 330 nm. These molecules disappear, giving rise to Hg_2Cl_2. The formation of HgCl molecules in the reduction of $HgCl_2$ has been demonstrated by electron paramagnetic resonance.[21] After γ-irradiation of frozen aqueous sulfuric acid solutions of this salt at 77 K, a signal due to the HgCl molecule is observed. Its quartet hyperfine structure is due to the interaction of the unpaired electron with the ^{35}Cl and ^{37}Cl magnetic nuclei, the nuclear spins of which are identical and equal to 3/2, while the magnetic moments are similar. In concentrated hydrochloric acid solutions (8 M), mercury is present in the form of the complex HgCl and the reduction of the mercury ion is not accompanied by the splitting off of chloride ions.[21] The formation of the HgBr[22] and HgI[23] molecules has been detected by pulse radiolysis in the reduction of the corresponding divalent mercury salts in aqueous solutions.

3. Ga^{2+}, In^{2+}, and Tl^{2+} ions and In and Tl atoms

The Ga^{3+} and In^{3+} ions are vigorously hydrolysed in aqueous solutions. It has been established that these ions and their hydrolysed forms are virtually not reduced by hydrogen atoms and the formation of the Ga^{2+} and In^{2+} ions, occurring in aqueous and neutral solutions, is a result of the interaction only with hydrated electrons.[24–26] The absorption band maxima of the Ga^{2+} and In^{2+} ions are at 268 and 263 nm respectively. The absorption spectrum of the indium aquo-complex in the +2 oxidation state is presented in Fig 1. The Tl^{2+} ion has been obtained in a strongly acid medium on reduction of trivalent thallium by hydrogen atoms.[27] Its absorption, the maximum of which occurs at wavelengths shorter than 225 nm, has been recorded. We may note that, together with the main absorption band, an additional shoulder appears for the hydroxo-complexes of divalent gallium[25] and thallium[27–30] — at 300 nm for the first complex and 360 nm for the second.

The Tl^+ ion is stable in aqueous solutions. The oxidation-reduction potential of the Tl^+/Tl^0 couple is -1.94 V, which implies

the possibility of its reduction by both hydrated electrons and hydrogen atoms in aqueous solutions. It has been shown [31] that this does indeed take place. Fairly concentrated salt solutions and long electron pulses (2 μs) were used in the experiments. As a consequence of the high rate of the reaction

$$Tl^0 + Tl^+ \rightleftarrows Tl_2^+,$$

the equilibrium constant of which is 2.3×10^3 litre mol^{-1}, the optical absorption due to thallium atoms was hardly observed owing to the intense absorption due to the Tl_2^+ species formed (a band with a maximum at 420 nm). Ershov *et al.*[32] refined the characteristics of the absorption spectrum of thallium atoms. A low concentration of Tl^+ ions (1×10^{-4} M) was used for this purpose, the solution containing also isopropyl alcohol as a hydroxyl radical scavenger. The spectrum was recorded 0.7 μs after the application of 15 ns or 0.5 μs electron pulses. Under these conditions, the equilibrium in the last reaction is displaced to the left. It was established that the absorption by Tl^0 (Fig. 2) includes two bands — at 450 nm ($\varepsilon = 5 \times 10^3$ litre mol^{-1} s^{-1}) and at 260 nm ($\varepsilon = 9 \times 10^3$ litre mol^{-1} s^{-1}).

The In^+ ion is unstable in aqueous solutions and is readily oxidised, forming In^{3+} ions. The calculated reduction potential of indium atoms in aqueous solution proved to be -2.3 V.[33] It is identical with the potential of hydrogen atoms. This means that In^+ ions could be reduced only by hydrated electrons. Aqueous InBr solutions were used in the above study.[33] In the presence of bromide ions, univalent indium becomes more stable. It has been established that the indium atoms arising immediately after the application of a 15 ns electron pulse are characterised by absorption bands with maxima at 500 nm and at a wavelength shorter than 300 nm. After a time, the intensities of the above bands fall and new bands appear at 310 and 460 nm. The rate of appearance of the latter increased with increase in the salt concentration in solution. The above changes were induced by the reaction

$$In^0 + In^+ \rightleftarrows In_2^+,$$

the equilibrium constant of which is approximately 5×10^2 litre mol^{-1}. We may recall that, in contrast to the metal atoms and ions examined above, having the $d^{10}s^1$ configuration, indium and thallium atoms are characterised by the $d^{10}s^2p^1$ electronic configuration.

4. Pb(I) and Pb(III) ions

Lead aquo-complexes in the +1 and +3 oxidation states were obtained when Pb^{2+} ions were reduced by hydrated electrons and oxidised by hydroxyl radicals in aqueous, neutral, and alkaline aqueous solutions. The Pb^+ ion is formed on pulse radiolysis in neutral or weakly acid Pb^{2+} solutions.[34–36] Its absorption spectrum is presented in Fig. 2. The ion has a $d^{10}s^2p^1$ outer electron shell and gives rise to a low-intensity absorption band at 320 nm ($\varepsilon = 2.5 \times 10^3$ litre mol^{-1} cm^{-1}). Divalent lead ions are readily hydrolysed in aqueous solutions. At pH 6 they already exist in the $PbOH^+$ form. The formation of the Pb^{3+} aquo-complex may therefore be expected only for acid aqueous solutions. Indeed the above ion is formed on oxidation of Pb^{2+} by hydroxyl radicals at pH < 4 in aqueous solutions saturated with N_2O.[37] Its absorption band, with a maximum at $\lambda < 220$ nm, extends into the UV region. At pH ~ 4 an additional weak shoulder is formed at 330 nm and is due to the hydroxo-complex PbOH. The pK value for the hydrolytic reaction

$$PbOH \rightleftarrows Pb^+ + OH^-$$

is 4.0. At pH > 6, an additional shoulder is also observed at 360 nm with the absorption band in the UV region.[38] The electrical conductivity of the solution does not change under these conditions, which suggests the following reaction:

$$PbOH^+ + OH \rightarrow Pb(OH)_2^+.$$

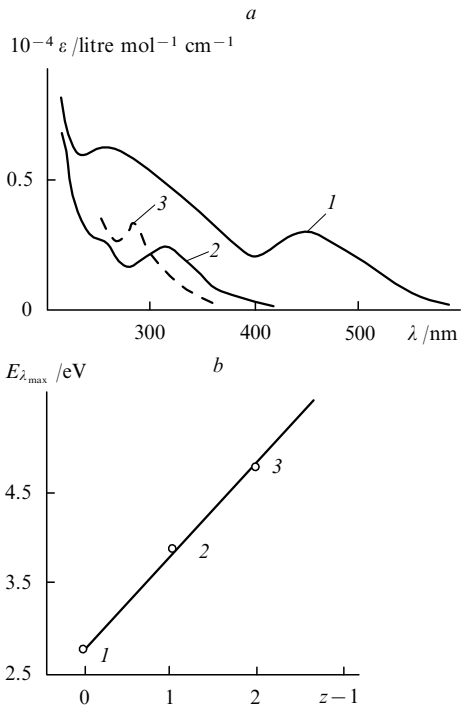


Figure 2. Optical absorption spectra of the atoms and ions of metals with the $d^{10}s^2p^1$ electronic configuration in water (*a*) and the dependence of $E_{\lambda_{max}}$, on the charge (*b*).
(*1*) Tl^0 (*2*) Pb^+; (*3*) Bi^{2+}.

At pH 11.4, divalent lead forms the hydroxo-complex $Pb(OH)_3^-$. The $Pb(OH)_4^-$ species probably arises in its interaction with the OH radical:

$$Pb(OH)_3^- + OH \rightarrow Pb(OH)_4^-.$$

Its absorption spectrum is characterised by a narrow band at 280 nm and a broader band at ~360 nm. The same species appears in the reduction of tetravalent lead in a highly alkaline solution (pH 13) by the reaction

$$Pb(OH)_6^{2-} + e_{aq}^- \rightarrow Pb(OH)_4^- + 2OH^-.$$

The complex $PbCl^{2+}$ has been obtained in the oxidation of Pb^{2+} ions (5×10^{-4} M) by hydroxyl radicals in neutral and acid aqueous solutions saturated with nitrous oxide and containing chloride ions (> 5×10^{-2} M).[39] The increase in the charge on the lead ion and the decrease in its radius compared with the Pb^{2+} ion led to the formation of a monochloride complex in the reactions

$$PbOH^{2+} + Cl^- \rightleftarrows PbCl^{2+} + OH^- \quad \text{at pH 6,}$$

$$Pb^{3+} + Cl^- \rightleftarrows PbCl^{2+} \quad \text{at pH 3.5.}$$

The pK values for the above equilibria are 1.2 and 2.6 respectively.

The optical absorption of the above complex includes four bands with $\lambda_{max} = 276$, 320, 380, and 485 nm, while the extinction coefficients are respectively 6.0×10^4, 3.1×10^4, 3.2×10^4, and 1.2×10^4 litre mol^{-1} cm^{-1}.

On the other hand, the PbCl molecule did not arise on reduction of lead(II) chloride complexes by hydrated electrons even at a chloride ion concentration of 0.1 M. The following reaction occurred under these conditions;

$$PbCl_3^- + e_{aq}^- \rightleftarrows Pb^+ + 3Cl^-.$$

Only in the presence of NaCl in the solution (~2 M) was the formation of PbCl observed (main absorption band at wavelengths less than 280 nm, additional bands at 300 and 390 nm). The instability constant of this complex (pK_i) was estimated as approximately -0.3.[39]

5. Bi(II) and Bi(IV) ions

Since bismuth is vigorously hydrolysed in aqueous solutions, concentrated perchloric solutions (up to 5 M) are used for its preparation in the initial Bi^{3+} form. Under these conditions, the hydrogen atoms formed after the application of an electron pulse reduce the Bi^{3+} ions to Bi^{2+} (single absorption band with a maximum at 285 nm).[40] No evidence for the possibility of the oxidation of Bi^{3+} by hydroxyl radicals and the formation thereby of Bi^{4+} ions was found. This reaction probably does not occur at all owing to the high oxidation potential of Bi^{4+}. Indeed, an estimate of this potential yields $\sim$3.5 V, which is significantly higher than the potential of the OH radical (2.9 V).

Ionic Bi(II) and Bi(IV) chloride complexes have been obtained by pulse irradiation of concentrated aqueous hydrochloric acid solutions.[41] The absorption due to the Bi(II) ion is characterised by two bands with maxima at 350 and 460 nm and that due to the Bi(IV) ion is characterised by bands at 270 and 370 nm.

IV. Atoms and ions of metals in unusual oxidation states in frozen aqueous solutions

The method for the preparation of metal ions in unusual oxidation states in frozen aqueous solutions is based essentially on the same reactions involving reduction by electrons, formed on ionisation of the medium, and oxidation by the hydroxyl radicals, arising in ion–molecule reactions of the positively charged H_2O^+ parent ions (see, for example, Ershov and coworkers [42, 43]). Concentrated aqueous solutions of a wide variety of electrolytes, for example, perchloric, sulfuric, hydrochloric, and other acids and their salts or alcohols, to which the metal salts investigated are added, are used for these purposes. On rapid freezing of such solutions in liquid nitrogen, transparent glasses, retaining to the maximum extent the structure of the liquid aqueous media, are formed. During exposure to ionising radiation (usually ^{60}Co γ-radiation), the metal ions are reduced by thermalised mobile electrons. The metal atoms or ions formed are stable indefinitely at 77 K. The oxidation reactions of the metals occur on raising the temperature to $\sim$150 K. At this temperature, the hydroxyl radicals localised in intermolecular traps become mobile. Many atoms and ions of metals in unusual oxidation states have been obtained and investigated in this way.[44–56]

It was found that the optical characteristics of the atoms and ions of metals with $d^{10}s^1$ or $d^{10}s^2p^1$ outer electron shells in aqueous solutions at room temperature and at the temperature of liquid nitrogen do not differ significantly. Only a 10–20 nm hypsochromic shift and some narrowing of the band are observed. The most significant results were obtained in the study of the ESR spectra of the metal atoms and ions in frozen aqueous media. Indeed, by means of the ESR method one can not only demonstrate the very fact that the atoms and ions in unusual oxidation states are formed but the structure of the paramagnetic centre, the nature of the environment, and the nature of the distribution of the unpaired electron can also be determined.

Metals usually have several isotopes, some of which may carry a nuclear spin. The paramagnetic ions formed on addition of a single electron to the outer *s* orbital are therefore characterised by the presence of two types of signals. The first are due to isotopes without nuclear spin and are represented in the ESR spectra by singlets in the region of the *g*-factor of the free electron. The second are due to isotopes carrying a nuclear spin and their ESR spectra are characterised by the presence of a hyperfine structure (HFS). Light elements (copper and silver) differ from others by the fact that the HFS constants of the ESR signals are small but sufficient for observation in the usual microwave spectrometer (magnetic field up to 300–1000 mT). For virtually all other elements, the HFS constants are so large that their resonance frequencies exceed the UHF field frequency employed in the ESR spectrometer. Only certain components of the HFS of the paramagnetic atom or ion are therefore observed. Fig. 3 presents the ESR spectra for the Ga^{2+} and Pb^{3+} ions. The HFS constants were calculated from the positions of the high-field components of the signals by the Breit–Rabi equation.[57] Table 1 presents the characteristics of the ESR spectra for a series of paramagnetic metallic species having an unpaired electron in the outer *s* shell. Evidently, the *g*-factor exhibits a negative deviation (Δg) relative to the *g*-factor of the free electron, which is 2.0023. A negative deviation of the *g*-factor is characteristic of paramagnetic centres with an ex excess electron. Furthermore, one may note that Δg increases in absolute magnitude along the subgroup and diminishes along one Period with increase in the atomic number of the element. In the former cases, the charge on the paramagnetic species is constant under these conditions, but the mass of the nucleus of the element increases (compare, for example, the equal-charge series, Zn^+, Cd^+, Hg^+), while in the latter case the paramagnetic species have the same electronic structure within the limits of the Period, but their charge increases under these conditions (compare the isoelectronic series Ag, Cd^+, Ga^{2+}, Sn^{3+}). The ratio A_{iso}/A^0_{iso}, which defines the density of the *s* state on the metal nucleus, increases within the limits of the equal-charge series of paramagnetic species with increase in the number of the Period. On the other hand, it diminishes within the limits of the isoelectronic series with increase in the charge on the ion.

Table 1. Characteristics of the ESR spectra of the atoms and ions of metals in the electronic state $^2S_{1/2}$ in a frozen aqueous solution at 77 K.[58–62]

Atom, ion	*g*-Factor	A_{iso}/mT [a]	A^0_{iso}/mT [b]	A_{iso}/A^0_{iso}
$^{63}Cu^0$			2094	
$^{67}Zn^+$			813	
$^{69}Ga^{2+}$		2260	5034	0.449
$^{77}Ge^{3+}$			1077	
$^{109}Ag^0$	1.9814	580	705	0.773
$^{111}Cd^+$	1.9896	3250	5137	0.633
$^{113}In^{2+}$			8139	
$^{117}Sn^{3+}$	1.9950	6825	15935	0.428
$^{197}Au^0$			1089	
$^{199}Hg^0$	1.9818	11350	14453	0.780
$^{203}Tl^{2+}$		43210	62622	0.690
$^{207}Pb^{3+}$	1.9920	16000	27796	0.575

[a] A_{iso} is the experimental isotropic HFS constant for the metal atom or ion in aqueous solution. [b] A_{iso}/A^0_{iso} is the isotropic HFS constant for the atom or ion in the free state.

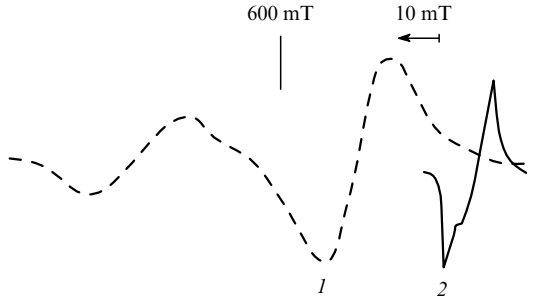


Figure 3. ESR spectra of Ga^{2+} ions at 77 K (*1*) and Pb^{3+} ions at 150 K (*2*) in a γ-irradiated $HClO_4$ solution (6 M).
Salt concentration: (*1*) 0.25 M $Ga(ClO_4)_3$; (*2*) 0.1 M $Pb(ClO_4)_2$.

V. Regularities in the variation of electronic properties

In the preparation and study of the properties of metals in unusual oxidation states, characterised by the presence of a single electron in the *s* or *p* orbitals, investigators always showed the greatest interest in the aquo-complexes of such metals. This is because the aquo-complexes are in fact most common and have been thoroughly investigated. The regularities in the variation of the fundamental properties of the above metals within the Periods and Groups of the Periodic System have been discovered.[51, 54–56, 63, 64] We shall deal with some of them. Metals in unusual oxidation states are extremely unstable and exist for a short time, so that the methods for their investigation are limited with the consequent limitation of the available information about their properties. These are in the first place the characteristics of their optical absorption and ESR spectra and the properties of their electronic structures as well as the oxidation-reduction potentials which follow from them.

1. Aquo-complexes

The absorption by the atoms and ions of metals with the $d^{10}s^1$ electronic configuration in an aqueous solution in the state of an aquo-complex is characterised by a single intense UV absorption band. The position of the band undergoes a smooth hypsochromic shift in an isoelectronic series of metals with increase in the charge on the species, as can be seen for the Ag^0, Cd^+, In^{2+} series (Fig. 1). We may note that the absorption band of the Sn^{3+} ion, the next member of the above isoelectronic series, is at $\sim$215 nm in a frozen aqueous solution at 77 K,[54] *i.e.* the tendency for the absorption to be displaced into the UV region with increase in the charge on the ion is continued. Furthermore, the energies of the optical transitions at the absorption band maxima ($E_{\lambda_{max}}$) increase linearly with increase in z (Fig. 4). In the subgroups, the energies increase with increase in the number of the Period. These regularities, discovered at an early stage of the study of the properties of metals,[51, 54–56] served as a basis for the prediction of the expected values of $E_{\lambda_{max}}$ for a series of atoms and ions which at that time had not yet been obtained. Thus the positions of the absorption bands were predicted and later determined experimentally for copper and gold atoms, Pb^{3+} ions, *etc*.

The optical absorption of the aquo-complexes of metals in the $^2S_{1/2}$ state is due to the $2a_{1g} \rightarrow 2t_{1u}$ transition. This transition can be regarded to a large extent as the transfer of an unpaired electron from the atomic orbital of the central metal ion to the mixed *np*, 2*s* and 2*p* orbital. The first optical transition in the same metal atoms and ions in the gas phase corresponds to the $S \rightarrow P$ transition. This entails the splitting of the level as a consequence of spin–orbit coupling. Thus in the case of silver atoms the energies corresponding to the $P_{1/2}$ and $P_{3/2}$ levels in the gas phase are respectively 338 and 328 nm. As mentioned above, in water a broad band with a maximum at 360 nm corresponds to silver atoms. This means that, on passing to an aqueous solution, the absorption band undergoes a 'red' shift and becomes significantly broader. For this reason, if the splitting due to spin–orbit coupling is not very marked, it is not observed. The differences between the energies of the $P_{1/2}$ and $P_{3/2}$ levels for the Ge^{3+}, Sn^{3+}, and Pb^{3+} ions in the gas phase are 0.346, 0.807, and 2.611 eV respectively.[65] If one bears in mind that the values of $E_{\lambda_{max}}$ for atoms and ions in the $^2S_{1/2}$ electronic state in aqueous solutions are in the range from 3 to 6 eV, one may conclude that the splitting of the energy levels may significantly complicate the structure of the bands in the spectra of the aquo-complexes. For elements of the Fourth and Fifth Periods, the above effect most probably leads to the broadening of the absorption bands, while in the case of the Sixth Period the splitting may prove to be considerable. Indeed, two absorption bands have been observed for Hg^+, at 225 and 255 nm,[17, 18] which is probably a consequence of the splitting of the *p* level.

The first optical transition in the aquo-complex corresponds to intracomplex oxidation. The validity of this conclusion is confirmed by the linear correlation between $E_{\lambda_{max}}$ and the $s^1 \rightarrow p^1$ excitation energies of the ions in the gas phase ($E_{s \rightarrow p}$) (Fig. 5). On the other hand, such correlation between $E_{\lambda_{max}}$ and the energy of the $d^{10}s^1 \rightarrow d^9s^2$ transition in the gas phase is not observed, which indicates that the optical transition in the aquo-complex is mainly due to the $s^1 \rightarrow p^1$ excitation.[63]

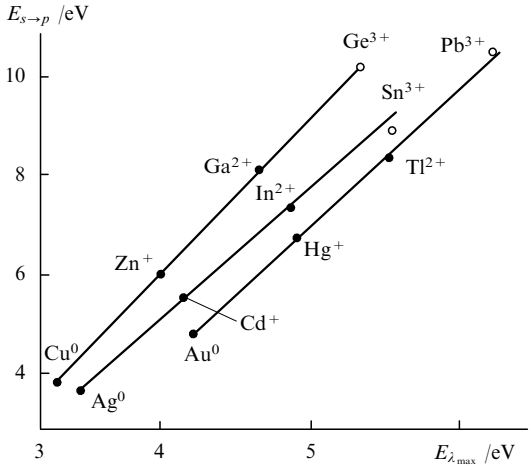


Figure 5. Dependence of $E_{s \rightarrow p}$ for the metal ion in the gas phase on $E_{\lambda_{max}}$ for the ion in the form of an aquo-complex.

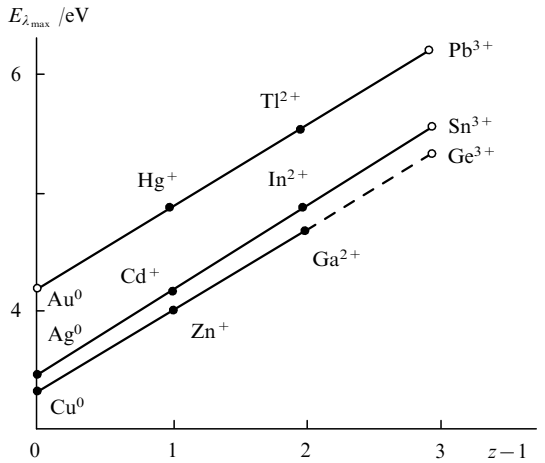


Figure 4. Dependence of $E_{\lambda_{max}}$ on the charge of the metal ion.

Analysis of spectroscopic data for the gas phase demonstrates the existence of the fundamental linear dependence of $E_{\lambda_{max}}$ on z of the type established for an aqueous medium.[63] The above relation has been justified theoretically[64] and equations relating the energies of the $s \rightarrow p$ transitions for hydrogen-like ions with a filled *d* shell to their charge have been derived. The approach is based on the familiar dependence of the energy term for a hydrogen-like ion on the charge. It is described by the Balmer formula, supplemented by relativistic corrections and the relations between the mass and the extent of spin–orbit coupling. Ultimately the following equation, relating the change of the electronic transition energy (expressed in rydbergs) for a hydrogen-like ion to its charge was obtained:

$$E_{ns \rightarrow np} = \frac{2K_n}{n^2} z + az + c, \qquad (1)$$

where n is the number of the electron shell and the quantities K_n, a, and c are determined by the shielding constants for the ions and

are found numerically from the dependences of their ionisation potentials in the gas phase on the charge z. For an isoelectronic series of ions, K_n is constant. Fig. 6 illustrates the dependences of the $s \rightarrow p$ transition energies for ions in the gas phase and in aqueous solution on z. They are linear and are described satisfactorily by Eqn (1). There is a slight deviation only for the first elements of the isoelectronic series, namely for copper, silver, and gold atoms. This is probably due to a certain degree of mixing of the s and d electronic states of these atoms. The constants a and c for an aqueous medium are the same as for the gas phase, but the quantities K_n differ significantly (Table 2). The intercept produced by the extrapolation of lines *1* and *2* on the ordinate axis is the same for the gas phase and aqueous solution. The intercept is determined by the constant c in Eqn (1). The physical significance of the constant is that of the energy of the $s \rightarrow p$ transition for an ion with $z = 0$.

Table 2. The coefficients K_n, a, and c of Eqn (1) for isoelectronic ions of the elements in the Fourth, Fifth, and Sixth Periods.

Period	K_n (gas phase)	K_n (aqueous phase)	a	c
4	0.862	0.221	0.035	0.165
5	0.994	0.318	0.031	0.188
6	1.311	0.312	0.042	0.234

Using the simple linear dependence of the $s \rightarrow p$ transition energy on the charge for a series of isoelectronic ions in the $^2S_{1/2}$ electronic states, it is possible to calculate by Eqn (1) or determine graphically (Fig. 6) any fundamental characteristics for ions which have not been obtained in this electronic state in the gas phase (Table 3). The energies of the optical transitions can be determined similarly also for ions in aqueous media. However, the existence of a whole series of these (for example, the As^{4+}, Sb^{4+}, Bi^{4+}, and other highly charged cations of the succeeding subgroup) is impossible because their oxidation potentials are higher than that of the hydroxyl radical.

Table 3. The values of $E_{s \rightarrow p}$ for a series of elements in the Fourth, Fifth, and Sixth Periods in the electronic state $^2S_{1/2}$.

z	Fourth		Fifth		Sixth	
	I[a]	II[b]	I[a]	II[b]	I[a]	II[b]
5	–	–	–	–	Po	12.5
6	Br	15.6	I	13.1	At	14.1
7	Kr	17.4	Xe	14.7	Rn	15.8

[a] Element. [b] Energy /eV.

Experimental data on the properties of metal ions having the $d^{10}s^2p^1$ electronic configuration are limited and are in essence confined to the In^0, Tl^0, Pb^+, and Bi^{2+} species. Nevertheless, it is possible to analyse the structure and positions of the optical absorption bands for the isoelectronic series of the above Sixth Period metal ions. Their optical absorption spectra and the dependence of $E_{\lambda_{max}}$ on the ionic charge (Fig. 2) show that the absorption band on the long-wavelength side shifts to the UV region in the Tl^0, Pb^+, Bi^{2+} series, while $E_{\lambda_{max}}$ increases linearly at the same time with increase in the ionic charge. For equally charged metal atoms in one subgroup (indium and thallium), a hypsochromic shift of the absorption band with increase in the number of the Period can be seen [λ_{max} is at 500 nm for In^0 (see Ref. 33) and at 440 nm for Tl^0 (see Ref. 32)]. Thus, similar regularities in the variation of the optical characteristics as a function of the positions of the elements in the Periodic System were observed both for the aquo-complexes of metals having one electron in the outer s orbital and for the aquo-complexes with an electron in the p orbital.

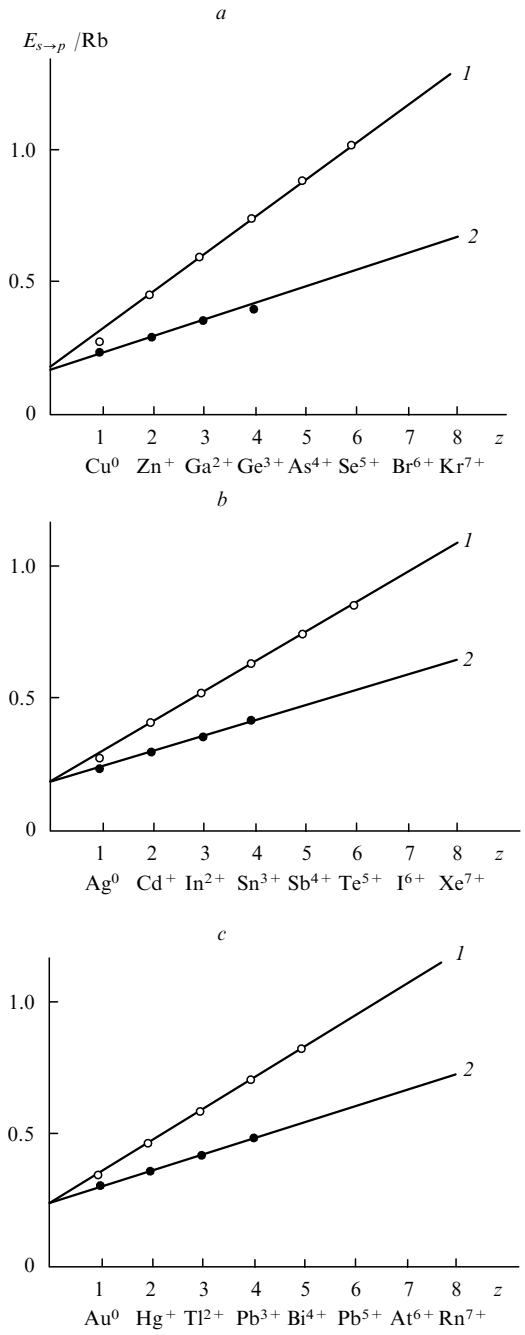


Figure 6. Dependence of the energy of the $s \rightarrow p$ transition on the charge z of the metal ions in the Fourth (*a*), Fifth (*b*), and Sixth (*c*) Periods. (*1*) In the gas phase; (*2*) in aqueous solution; circles — experiment; lines — calculation by Eqn (1).

2. Hydroxo-complexes

The incorporation of one OH^- ion in the coordination sphere of the metal ion leads to the splitting of the energy levels, which entails a change in the structure of the optical absorption spectrum. Apart from the main symmetrical absorption band, characteristic of the metal ion in the form of the aquo-complex, an additional broad band on the long-wavelength side is observed, as noted above. Fig. 7 presents a schematic arrangement of the energy levels for an octahedral complex, illustrating the nature of the changes in the structures of the optical transitions for mono- and di-hydroxo-complexes. The replacement of one or two water

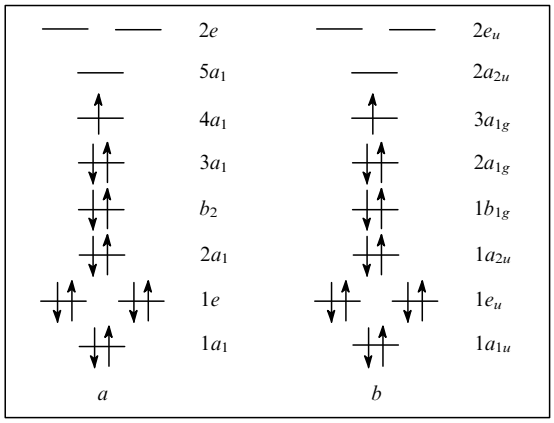


Figure 7. Schematic illustration of the energy levels for monohydroxo-complexes (*a*) and dihydroxo-complexes (*b*).

molecules by hydroxide ions respectively in position 1 (C_{4v} symmetry) or 1 and 4 (D_{4h} symmetry) leads to the splitting of the $2t_{1u}$ level. The existence of an additional transition in the hydroxo-complex is associated with a decrease in symmetry as a consequence of the appearance of new ligands. The $2t_{1u}$ level is split in such a way that the $2e$ level for $MOH^{(z-1)+}$ and the $2e_u$ level for $M(OH)_2^{(z-2)+}$ are determined by the interaction with water molecules and the energies of the $4a_1 \rightarrow 2e$ and $3a_1 \rightarrow 2e_u$ transitions respectively therefore change little compared with the energies $2a_{1g} \rightarrow 2t_{1u}$ transitions in the aquo-complexes. On the other hand, the $5a_1$ level for $MOH^{(z-1)+}$ and the $2a_{2u}$ level for $M(OH)_2^{(z-2)+}$ are associated predominantly with the interaction with OH^- ions, while the energies of the $4a_1 \rightarrow 5a_1$ and $3a_{1g} \rightarrow a_{2u}$ transition are respectively smaller than the energies of the transition observed in the aquo-complexes. It is noteworthy that in the monohydroxo-complex there is a possibility of the splitting or broadening of the band owing to the *trans*-effect. However, in the mono- and di-hydroxo-complexes, not only the nature of the disposition of the levels but also the energies of the corresponding optical transitions are fairly similar. For example, the same structures of the optical bands have been observed for the $TlOH^+$ and $Tl(OH)_2^0$ species.[28–30]

Figure 8 presents the dependence of $E_{\lambda_{max}}$ on z for the $4a_1 \rightarrow 2e$ and $4a_1 \rightarrow 5a_1$ transitions for the monohydroxo-complexes of Sixth Period metals. The long-wavelength component of the optical absorption band has been recorded for the $TlOH^+$ and $PbOH^{2+}$ ions and it has been stated that the maxima are located at $\lambda < 220$ nm and $\lambda < 240$ nm respectively. For HgOH, use was made of the results of a study [19] in which an additional absorption band, not found previously,[18] had been observed at 360 nm. It is seen from the figure that the linearity of the dependence of the energy at the absorption maximum on z, characteristic of the aquo-complexes, holds also for the hydroxo-complexes. The difference between the transition energies in the case of the hydroxo-complexes tends to increase with increasing z, *i.e.* the splitting of the $4a_1$ and $2e$ levels increases with increase in the charge and with decrease in the size of the central ion.

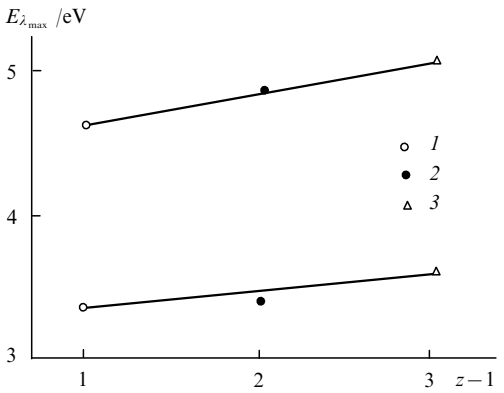


Figure 8. Dependence of $E_{\lambda_{max}}$ on the ionic charge for metal hydroxo--complexes.
(*1*) $HgOH^0$; (*2*) $TlOH^+$; (*3*) $PbOH^{2+}$.

For the fully substituted hydroxo-complexes, containing only hydroxide ions in their coordination sphere, the structure of the optical transitions is the same (with retention of the coordination numbers) as that for the aquo-complexes. The amount of experimental data for the above complexes is insufficient to establish quantitative relations. However, it is quite sufficient to demonstrate that the nature of the regularities characteristic of the aquo-complexes is retained. Thus the values $E_{\lambda_{max}} = 380$,[66] 340,[66] 280,[25] 275,[26] and 280 and 360 nm[35] have been found for the Zn(I), Cd(I), Ga(II), In(II), and Pb(III) hydroxo-complexes respectively. It is seen from the data presented that the optical transition energy increases with increase in z for isoelectronic ions. It also increases for equally charged ions with increase in the atomic number of the element. The decrease in the energy of the $2a_{1g} \rightarrow 2t_{1u}$ optical transition energy when water molecules are substituted by hydroxide ions is correlated with the decrease in the ionisation potentials on passing from H_2O to the OH^- ion.

3. Halide complexes

The principal characteristics of the optical transitions in the fully substituted chloride complexes of Group II – IV metals in the $^2S_{1/2}$ electronic state have been investigated by Aleksandrov *et al.*[55] HCl solutions (6 – 10 M), to which salts of the test metals had been added, were employed. On freezing, they gave rise to transparent glasses. After γ-irradiation at 77 K, the reduced metal ions in the $^2S_{1/2}$ electronic state appeared and their optical absorption spectra were measured in a Dewar vessel at liquid nitrogen temperature. It was established that the structure of the optical absorption is significantly more complex than the analogous structure observed for the aquo-complexes. Two – three absorption bands are observed for the metals in the Fifth and Sixth Periods. For an isotypical electronic transition, the energy at the absorption band maximum diminishes with increase in the charge on the metal ion. As stated above, similar data have been obtained by pulse radiolysis for metal halide complexes in liquid aqueous solutions. Fig. 9 presents a schematic illustration of the energy levels for a monohalide complex having C_{4v} symmetry. Compared with the schemes examined for the aquo- and hydroxo-complexes, here additional ligand molecular orbitals (MO), made up of the πp and σp atomic orbitals of the ions X^-, are present. According to this scheme, the allowed transitions in the $M(H_2O)_5X^{(z-1)+}$ complex

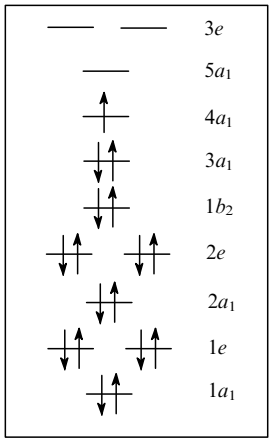


Figure 9. Schematic illustration of the energy levels for monohalide complexes.

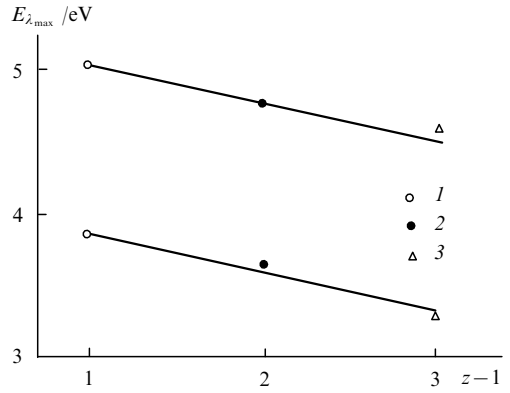


Figure 10. Dependence of $E_{\lambda_{max}}$ on the ionic charge for metal monochloride complexes.
(*1*) $HgCl^0$; (*2*) $TlCl^+$; (*3*) $PbCl^{2+}$.

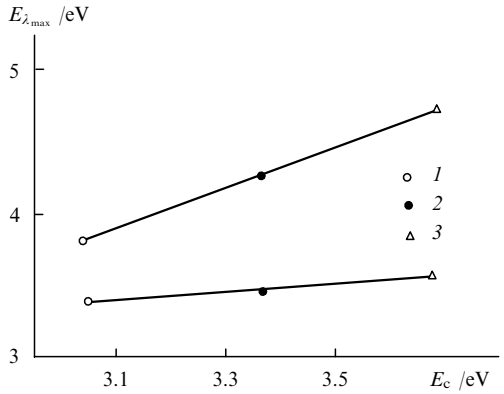


Figure 11. Dependence of $E_{\lambda_{max}}$ for monovalent mercury halide compounds on the electron affinity (E_a) of the halogen atom.
(*1*) HgI; (*2*) HgBr; (*3*) HgCl.

are $4a_1 \rightarrow 5a_1$ and $4a_1 \rightarrow 3e$, as well as the new transitions $2e \rightarrow 4a_1$ and $1b_2 \rightarrow 4a_1$.

Figure 10 presents the dependence of the optical transition energies for the monochloride complexes of Sixth Period metals — mercury, thallium, and lead, containing one additional electron, *i.e.* in the $^2S_{1/2}$ electronic state. Evidently, in contrast to the analogous relations for the aquo- and hydroxo-complexes, $E_{\lambda_{max}}$ for the chloride complexes diminishes with increase in the degree of oxidation z. This factor permits the conclusion that the optical bands of $MCl^{(z-1)+}$ are determined by the $2e \rightarrow 4a_1$ and $1b_2 \rightarrow 4a_1$ transitions. The molecular orbitals $2e$ and $1b_2$ are predominantly due to ligand molecules, *i.e.* they are occupied by the electrons of the chloride ions. For metals in isoelectronic series, the energy of the abstraction of an electron increases with increase in the charge. This means that the $4a_1$ level, at which the electron is located, is lowered with increase in z. On the other hand, the $2e$ and $1b_2$ levels, at which the nonbonding electron pairs of the Cl ions are located, hardly change their positions. The energies of the above transitions in the $MCl^{(z-1)+}$ complexes in an isoelectronic series therefore decrease with increase in the degree of oxidation. The proposed model describes correctly the experimental dependence $E_{\lambda_{max}}$ on z. In contrast to the aquo- and hydroxo-complexes in which an electron is transferred from the metal ion to the ligand molecules, in the halide complexes the electron is actually transferred from the ligand to the metal. This is the reason for the opposite type of dependence of $E_{\lambda_{max}}$ on z for the chloride complexes of metals in the electronic state $^2S_{1/2}$ compared with the aquo-complexes.[55]

For $PbCl^{2+}$, four optical absorption bands are observed.[39] This finding may be attributed to a relativistic effect. The allowed transitions at the $^2P_{1/2}$ and $^2P_{3/2}$ levels differ, as already stated, by 2.6 eV. As a consequence of this, each of the $2e \rightarrow 4a_1$ and $1b_2 \rightarrow 4a_1$ transitions undergoes additional splitting. The energies of all the transitions in the $PbCl^{2+}$ complex are 4.56, 3.85, 3.20, and 2.54 eV.[39] The difference between the transition energies for paired groups of bands is indeed close to the expected value. For lighter elements, the splitting is significantly smaller and the relativistic effect is therefore manifested by a broadening of the absorption band.

For molecular monovalent mercury halide complexes (HgCl, HgBr, and HgI), two absorption bands are observed in each case, their positions undergoing a hypsochromic shift with increase in the mass (atomic number) of the halogen. Thus, whereas the absorption bands for HgCl are at 245 and 330 nm,[20] they are at 280 and 350 nm for HgBr [22] and at 320 and 360 nm for HgI.[23] Such variations in the energies are consistent with the proposed energy level scheme. Indeed, the electron affinity of halogen atoms diminishes in the Cl – Br – I series, which corresponds to a rise in the positions of the $2e$ and $1b_2$ levels. When the position of the $4a_1$ level, which represents predominantly the atomic orbital of the metal, is retained, this should lead to a decrease in the energies of the $2e \rightarrow 4a_1$ and $1b_2 \rightarrow 4a_1$ transitions in the HgCl – HgBr – HgI series, which does in fact occur. Furthermore, there is a strict linear relation between $E_{\lambda_{max}}$ the above monovalent mercury halides and the electron affinity of the halogen atom (Fig. 11).

VI. Oxidation-reduction potentials

The direction and effectiveness of a reaction involving electron transfer is determined by the oxidation-reduction potentials of the reactants participating in it. The potential of the reaction between a reductant B^- and an oxidant O, *i.e.*

$$B^- + O \rightleftarrows B + O^-$$

may be determined from the equilibrium constant of the reaction $K = k_+/k_-$ (here k_+ and k_- are the rate constants for the forward and reverse reactions). Metal ions in unstable oxidation states are extremely reactive and the rates of reactions with their participation are as a rule controlled by diffusion. The reactions are irreversible. The rate constants for the reverse reactions cannot usually be determined. For this reason, approximate theoretical and experimental methods are used to determine the oxidation-reduction potentials. In a theoretical calculation, it is postulated [67] that the energy of hydration of a metal ion in an unusual oxidation state depends on its radius in the same way as for alkali metal ions and the radius itself is equal to the average radius of the element preceding the given metal and that of the radius which follows it in stable oxidation states.

The experimental approach involves comparison of the characteristics of the reactions involving the reduction of particular metal ions by various radical reductants with known potentials. The potential is then estimated as the average of the potential of a reactant which led to the reduction of the metal ion and that of a reactant the presence of which did not lead to reduction. Problems concerning the determination of the oxidation-reduction potentials of metal ions in unusual oxidation states were discussed in greater detail in our earlier review.[1]

Table 4 presents the potentials known hitherto for metal ions with the $d^{10}s^1$and $d^{10}s^2p^1$ electronic configurations. The standard potentials of metal couples in stable oxidation states [$E^0(M^{z+}/M)$] as well as the analogous oxidation reduction potentials or metal couples in the atomic state [$E^0(M^{z+}/M^0)$] are also presented for comparison. In the latter case, account was taken of the correction for the energy of their sublimation at room temperature.[68] It is striking that noble metals (copper, silver, and gold) in the atomic state ($d^{10}s^1$ electronic configurations) are very powerful reductants. This is due to the presence of unpaired electrons in their outer *s* orbitals.

Table 4. The oxidation-reduction potentials E^0 /V.

Element	z	$E^0(M^{z+}/M)$	$E^0(M^{z+}/M^0)$	$E^0(M^{z+}/M^{(z-1)+})$
Cu	+1	+0.52	−2.6	
Zn	+2	−0.76	−1.25	−2.3
Ga	+3	−0.53	−1.36	−0.63
Ag	+1	+0.8	−1.8	
Cd	+2	−0.4	−0.81	−1.8
In	+3	−0.4	−1.05	−0.45
Sn	+2	−0.14	−1.53	
Sn	+4	+0.01	−0.67	+0.7
Au	+1	+1.65	−1.5	
Hg	+2	+0.85	+0.68	−1.5
Tl	+1	−0.34	−1.9	
Tl	+3	+0.72	+0.2	+0.3
Pb	+2	−0.126	−0.96	
Pb	+4	+0.78	+0.36	+1.8
Bi	+3	+0.22	−0.29	

In isoelectronic series of metals, one can trace a tendency towards a decrease in potential with increase in the charge of the metal ion. Fig. 12 illustrates graphically this relation. It is seen that in each of the series of the Fourth – Sixth Periods the potential diminishes with increase in z. Whereas at the beginning of the Period copper, silver, and gold atoms are fairly powerful reductants, the metal ions at the end of the isoelectronic series, namely trivalent tin and lead, exhibit the properties of powerful oxidants. Within the limits of a subgroup, *i.e.* for equally charged ions, the potential $E^0(M^{z+}/M^{(z-1)+})$ increases steadily with increase in the number of the Period. The established type of variation of $E^0(M^{z+}/M^{(z-1)+})$ in Periods and Groups makes it possible to predict or revise the potentials for metals the oxidation-reduction characteristics of which have not been investigated. Thus, by extrapolating the linear section of the relation between the potential and the charge of the Bi^{4+} cation, it is possible to determine the potential $E^0(Bi^{4+}/Bi^{3+})$. It was found to be approximately +3.5 V, which appreciably exceeds the oxidation potential of hydroxyl radicals (2.9 V). This explains the fact, mentioned above, that OH radicals are not able to oxidise Bi^{3+} ions in highly acid aqueous solutions.

Comparison of the metal potentials $E^0(M^{z+}/M^{(z-1)+})$ with the standard potentials and the potentials for the atomic state (Table 4) showed that their variations as a function of the charge z differ significantly. For one-electron oxidation ($d^{10}s^1 \rightarrow d^{10}s^0 + e^-$), a monotonic increase in the potentials with increasing z may be traced for all the Periods. This means that the stability of aquo-complexes of metals in oxidation states characterised by the electronic configuration $d^{10}s^1$ increases with increase in the number of the element in the Period. On the other hand, the variations of the standard potentials of these metals are not monotonic and reflect a complex dependence of the energies of abstraction of electrons on the degree of filling of the electron shells of the element as their number increases.

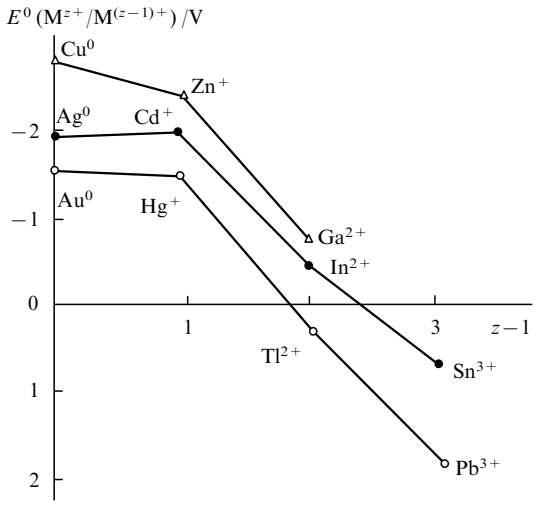


Figure 12. Dependence of $E^0(M^{z+})/M^{(z-1)+})$ on the charge z for metal aquo-complexes.

If one begins with the fact that the optical transition in an aquo-complex represents intracomplex oxidation of the metal ion, one may expect that the oxidation potential $E^0(M^{z+}/M^{(z-1)+})$ is correlated with the optical transition energy $E_{\lambda_{max}}$. Such correspondence does indeed exist (Fig. 13). The higher the value of $E_{\lambda_{max}}$ the more difficult it is to abstract an electron from the metal ion and the higher the oxidation potential of the latter. The correlation between $E_{\lambda_{max}}$ and $E^0(M^{z+}/M^{(z-1)+})$ for the aquo-complexes is justified when they have the same structure and retain it as the degree of oxidation is changed. A coordination number of 2 and a linear configuration of the complexes $M(H_2O)_2$ are characteristic of the elements of the copper subgroup.[69] It may be expected that the coordination number of the elements of the next subgroup (Zn, Cd, and Hg) is six, although the aquo-complex of divalent mercury may be distorted.[69] High coordination numbers (5 or 6) may also be characteristic of the trivalent aquo-complexes in the gallium subgroup. Thus aqueous solutions of indium ions contain the complexes $In(H_2O)_5OH^{2+}$ and $In(H_2O)_4(OH)$.[70] A coordination number of 6 is also characteristic of the elements of the germanium subgroup in the +4 oxidation state. Thus the most probable coordination number of the majority of the elements considered is 6. The copper subgroup is an exception and, as can be seen from Figs. 12 and 13, this fact is apparently the reason why a deviation from the linear relation between $E^0(M^{z+}/M^{(z-1)+})$ and $E_{\lambda_{max}}$ is observed for copper, silver, and gold atoms.

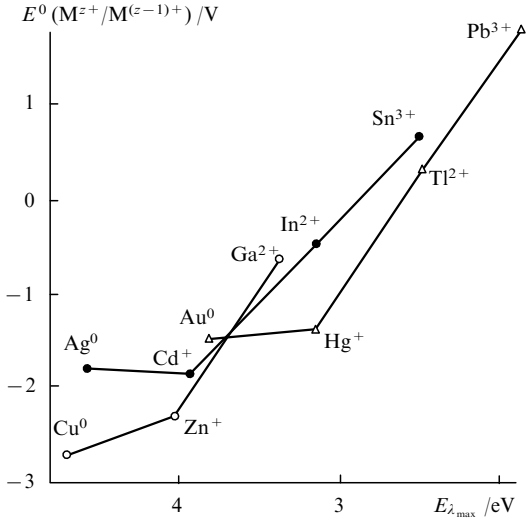


Figure 13. Dependence of $E^0(M^{z+})/M^{(z-1)+})$ on $E_{\lambda_{max}}$ for metal aquo-complexes.

It is noteworthy that the correlation of $E_{s \rightarrow p}$ and $E_{\lambda_{max}}$ (Fig. 5) makes it possible to determine from the dependence of $E_{s \rightarrow p}$ on $E^0(M^{z+}/M^{(z-1)+})$ the oxidation potentials of the aquo-complexes of metals in the electronic state $^2S_{1/2}$ for which there are some kind of data concerning the positions of their absorption bands. The above approach has been used widely in the case of f elements, for which the energies of the $f^n \rightarrow f^{n-1}d^1$ transitions in the gas phase are correlated with the oxidation potentials in aqueous solution.[71] The potentials E^0 of processes of the type $Zn^+ + e^- \rightarrow Zn^0$ are correlated with the energies of bands

determined by transitions from the ligand orbitals ($e_g \rightarrow t_{1u}$, *etc.*). They should occur in the short-wavelength region ($\lambda_{max} < 200$ nm)

Data referring to metal ions with the $d^{10}s^2p^1$ configuration are available only for elements of the Sixth Period (Tl^0, Pb^+, and Bi^{2+}). By analysing the data in Table 4 for these elements, one may conclude that a similar relation, involving a decrease in the potential with increase in the charge of the cation exists for them as well.

VII. Regularities in the variation of the dissociation constants of complexes

The change in the degree of oxidation of a metal ion is accompanied by a change in its charge and size. Despite the short time during which the ion exists in an unusual oxidation state, the corresponding equilibrium coordination sphere is formed in aqueous solution. The dissociation constants of isotypical complexes of metal ions, in different oxidation states, are different. The first hydrolysis constants have been determined for many ions with the $d^{10}s^1$ and $d^{10}s^2p^1$ configurations. These constants have been compared [72] with the corresponding constants for stable valence forms of the same metals.[73] It was established that the nature of the variation of the hydrolysis constants is consistent with the nature of the variation of these quantities predicted by electrostatic theory [74, 75] both for isoelectronic metal ions in the usual and unusual valence forms and for the same metals in different oxidation states. The stability of a complex is known [74, 75] to be determined by the potential energy of the interaction of two ions, which is proportional to the ratio $z_M z_L/r$, where z_M and z_L are respectively the charges on the metal ion and the ligand and r is the distance between them. Fig. 14 illustrates the variation of the first hydrolysis pK with the ratio z/r, where $z = z_M$, since the charge on the ligand (the OH^- ion) is -1 and $r = r_M + r_{OH^-}$. Evidently, the pK for isoelectronic ions in stable oxidation states, having the $d^{10}s^0$ electronic configuration, decreases linearly with increase in z/r. For elements of the Fourth and Fifth Periods, the slopes of the relations are almost the same, whilst for the elements of the Sixth Period they are significantly smaller. For metals in unstable oxidation states having the $d^{10}s^1$ electronic configuration, a similar relation is observed. However, in this case pK increase with decrease in the degree of oxidation of the metal. For example, pK increases in the sequence $Hg^+ \rightarrow Hg^{2+}$, $Tl^{2+} \rightarrow Tl^{3+}$, *etc.* The variation of the pK for isoelectronic series of ions in stable and unstable oxidation states is described satisfactorily by the simple equation

$$pK = \frac{q}{r} z + w, \qquad (2)$$

The coefficients q and w are listed in Table 5.

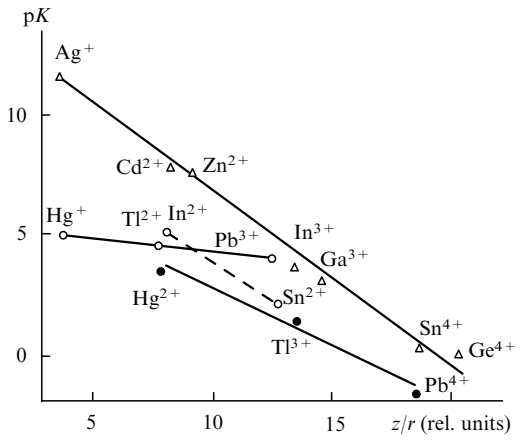


Figure 14. Dependence of the first hydrolysis constant on z/r.

Table 5. The coefficients q and w in Eqn (2).

Period	Electronic configuration	q	w
4	$d^{10}s^0$	$-0.74 + 0.2$	$14.2 + 0.5$
5	$d^{10}s^0$	$-0.74 + 0.2$	$14.2 + 0.5$
5	$d^{10}s^1$	$-0.65 + 0.1$	$10.0 + 1.0$
6	$d^{10}s^0$	$-0.49 + 0.02$	$7.7 + 0.4$
6	$d^{10}s^1$	$0.13 + 0.01$	$5.8 + 0.2$

The above characteristics of the variation of the pK with z/r agree with the concept of the decisive contribution of electrostatic interaction of the central ion and the ligand to the stability of the complex. For equally charged ions, the nature of the observed relations is more of an indication of the decisive role of the electronic structure. For example, a clear-cut sequence based on the increase in the pK with increasing atomic number of the element has been observed for the elements of the Sixth Period ($Hg^+ < Tl^+$, $Hg^{2+} < Tl^{2+} < Pb^{2+}$, $Tl^{3+} < Pb^{3+}$). However, for elements of the Fourth and Fifth Periods, the above relation is reversed ($Zn^{2+} > Ga^{2+}$, $Cd^{2+} > In^{2+} > Sn^{2+}$, $In^{3+} > Sn^{3+}$). Finally, one should note that the variation of the pK for equally charged ions in one subgroup is apparently not systematic (in particular, this was indicated earlier by Nazarenko *et al.*[73]). Thus the pK of Group III elements diminish in the sequences $In^{3+} > Ga^{3+}$, Tl^{3+} and $In^{2+} > Ga^{2+} > Tl^{2+}$, while for Group II elements they decrease in the sequence $Cd^{2+} > Zn^{2+} > Hg^{2+}$.

Bearing in mind the regularities established in the variation of the pK with z/r in isoelectronic series of metals of one Period and also the nature of the variation of this quantity in equal-charge series, it appears possible to estimate the pK for certain ions. Thus $pK = 11.1 \pm 0.5$ and 6.0 ± 0.5 can be obtained for Cu^+ and Au^+ respectively by Eqn (2) from the coefficients q and w found for the corresponding Periods. The pK for the Zn^+ and Cd^+ ions are apparently very similar and are in the range 7–9.

Regularities in the variation of the instability constants, expected from electrostatic theory, have also been observed for the chloride complexes of metals in different oxidation states, including the unstable states with the $d^{10}s^1$ and $d^{10}s^2p^1$ electronic configurations.

Constant	$TlCl$	$TlCl^+$	$TlCl^{2+}$	$PbCl$	$PbCl^+$	$PbCl^{2+}$
pK_i	0.5	4.6	7.7	-0.3	1.5	2.6

Evidently the constants increase with increasing charge on the metal ion. For lead compounds, a nearly linear variation of pK_i with z/r has been noted.[39] For thallium complexes, pK_i is appreciably higher.[76] This means that the stability of the complexes is influenced significantly by the nature of the central ion.

VIII. Conclusion

The formation of metal ions in unusual oxidation states is not characteristic solely of aqueous media. They arise also in inorganic oxide glasses doped with thallium, cadmium, lead, or other metals as a result of oxidation-reduction reactions initiated by ionising radiation, light, or mechanical action (see, for example, the review of Aleksandrov *et al.*[77]). The rigid structure of glasses is responsible for the indefinite stability of such ions. The decisive role of cooperative oxidation-reduction processes, the effectiveness and direction of' which depend on the composition of the glass and its structure and the presence of free and multicentre bonds in it, has been demonstrated. It is important to note that a series of regularities which have been observed for aqueous solutions and are discussed in detail in the present review (for example, the distribution of electron densities and the optical transition energies in the isoelectronic and equal-charge series of metals) are characteristic also of inorganic oxide glasses. On the

one hand, this makes it possible to assume that the observed regularities in fundamental properties are common to all metals in unusual oxidation states and, on the other, one may assume their practical importance in the development of glass compositions with specified characteristics.

At intermediate stages of oxidation-reduction reactions in aqueous solutions, containing the ions of several metals, short-lived mixed clusters may arise. Thus, various monovalent ions, such as Cd^+, Co^+, Zn^+, and Ni^+, generated on pulse irradiation with electrons, can react with the Ag^+ ions present in the solution.[16,78] The Zn^+ ion, which has a high reduction potential, enters under these conditions into a reaction with Ag^+ involving electron transfer and the formation of a silver atom. The Cd^+ and Co^+ ions, the potentials of which are close to that of atomic silver, form the mixed clusters $(CdAg)^{2+}$ and $(CoAg)^{2+}$. These cluseters exist only for several microseconds and decompose rapidly with formation of Cd^{2+} (or Co^{2+}) and the Ag_2^+ cluster. In the case of Ni^+, neither electron transfer in the reaction with the Ag^+ ion nor the formation of a simple mixed cluster have been established. However, silver is reduced with formation of a mixed product (possibly a larger mixed cluster), which appears when Ni^+ ions vanish. The appearance of mixed short-lived $(AgTl)^+$ and $(TlCd)^{2+}$ clusters was observed [79] in a study of the reactions of Tl_2^+ with Ag^+ and Cd^{2+} ions. The Pb^{2+} ion is reduced by Tl_2^+ with formation of the Pb^+ ion. The results obtained indicate the important, and sometimes the decisive, role of impurity ions as regards the direction or effectiveness of oxidation-reduction reactions.

Processes involving the reductive nucleation of metals (silver,[9,80,81] copper,[82,83] cadmium,[84] lead,[36] palladium,[85,86] *etc.*) are associated with the initial stage involving the formation of ions in unusual oxidation states and with their dimerisation or disproportionation reaction. The chain of consecutive growth of clusters ultimately leads to the appearance of subcolloidal and then colloidal metal particles. The nucleation of silver in polymer membranes,[87,88] in gelatin,[89] and on the surface of colloidal silicon [90] proceeds via a similar mechanism.

Certain special questions concerning the role of the anomalous valence forms of metals in catalysis have been examined in recently published reviews.[91–93]

Thus the studies on the preparation of short-lived metal ions in unusual valence states initiated about 30 years ago have now developed further. The use of pulse radiolysis and also of the technique involving the matrix isolation of chemically reactive species made it possible not only to confirm the possibility of the appearance of these short-lived species in aqueous solutions at intermediate stages of oxidation-reduction reactions but also to investigate comprehensively their properties. In the subsequent period, main efforts were directed towards the comparative analysis of these properties and their changes within Periods and Groups of the Periodic System. This has been done most thoroughly for simple complexes of Group I–V metals in the electronic state $^2S_{1/2}$ in aqueous solutions. In particular, a regular feature of the variation of the fundamental physicochemical properties of metal atoms and ions with the $d^{10}s^1$ electronic configuration which had not been known beforehand was established and theoretically justified. It consists in the fact that the resistance of the aquo-complexes of the above metals to oxidation and also the energies of the first electronic transitions increase monotonically with increase in the ionic charge within the limits of an isoelectronic series. These and other regular features discovered apparently reflect a fundamental property of the elements, namely the monotonic variation of their physicochemical characteristics within the limits of one Period. The possibility of predicting new unusual valence forms of the elements and their properties on the basis of regular features already established is thereby justified.

References

1. B G Ershov *Usp. Khim.* **50** 2137 (1981) [*Russ. Chem. Rev.* **50** 119 (1981)]
2. A K Pikaev, S A Kabakchi, I E Makarov, B G Ershov *Impul'snyi Radioliz i Ego Primenenie* (Pulse Radiolysis and Its Application) (Moscow: Atomnaya Energiya, 1980)
3. G V Buxton, C L Greenstock, W P Helman, A B Ross *J. Phys. Chem. Ref. Data* **17** 513 1988
4. J Butler, A Henglein *Radiat. Phys. Chem.* **15** 603 (1980)
5. H A Schwarz, R W Dodson *J. Phys. Chem.* **93** 409 (1989)
6. G V Buxton, R H Sellers *Coord. Chem.* **22** 195 (1977)
7. J Pukies, W Roebke, A Henglein *Ber. Bunsenges. Phys. Chem.* **72** 862 (1968)
8. R Tausch-Treml, A Henglein, J Lilie *Ber. Bunsenges. Phys. Chem.* **82** 1335 (1978)
9. B G Ershov, E Janata, A Henglein, A Fojtic *J. Phys. Chem.* **97** 4589 (1993)
10. N L Sukhov, M A Akinshin, B G Ershov *Khim. Vys. Energ.* **20** 392 (1986) [a]
11. A S Ghosh-Mazumdar, E Hart *Adv. Chem. Ser.* **81** 193 (1968)
12. S Mosseri, A Henglein, E Janata *J. Phys. Chem.* **93** 6791 (1989)
13. A Barkatt, J Rabani *J. Phys. Chem.* **79** 2592 (1975)
14. J Rabani, W A Mulac, M S Matheson *J. Phys. Chem.* **81** 99 (1975)
15. G W Buxton,R M Sellers *J. Chem. Soc., Faraday Trans. 1* 558 (1975)
16. B G Ershov, E Janata, A Henglein *J. Phys. Chem.* **98** 7619 (1994)
17. S Fujita, H Horii, S Taniguchi *J. Phys. Chem.* **77** 2868 (1973)
18. S Fujita, H Horii, T Mori, S Taniguchi *J. Phys. Chem.* **79** 960 (1975)
19. A K Pikaev, G K Sibirskaya, V I Spitsyn *Dokl. Akad. Nauk SSSR* **224** 638 (1975) [b]
20. N B Nazhat, K-D Asmus *J. Phys. Chem.* **77** 614 (1977)
21. A I Aleksandrov, B G Ershov *Izv. Akad. Nauk SSSR, Ser. Khim.* 249 (1976) [c]
22. S Fujita, H Horii, T Mori *Bull. Chem. Soc. Jpn.* **49** 1250 (1976)
23. S Fujita, H Horii, T Mori *Chem. Lett.* 865 (1976)
24. N L Sukhov, I E Makarov, B G Ershov *Khim. Vys. Energ.* **12** 375 (1978) [a]
25. N L Sukhov, B G Ershov *Khim. Vys. Energ.* **13** 55 (1979) [a]
26. N L Sukhov, B G Ershov *Khim. Vys. Energ.* **17** 113 (1983) [a]
27. H A Schwarz, D Comstock, J R Yandell, R W Dodson *J. Phys. Chem.* **78** 488 (1974)
28. M Vonifacic, K-D Asmus *J. Chem. Soc., Faraday Trans.* **20** 2074 (1976)
29. P O'Neill, S Steenken, D Schulte-Frohlinde *Angew. Chem.* **87** 417 (1975)
30. P O'Neill, S Steenken, D Schulte-Frohlinde *Angew. Chem., Int. Ed. Engl.* **14** 430 (1975)
31. B Cercek, M Ebert, A Swallow *J. Chem. Soc., A* 612 (1966)
32. B G Ershov, E Janata, A Henglein *J. Phys. Chem.* **98** 10891 (1994)
33. N L Sukhov, B G Ershov *Izv. Akad. Nauk SSSR, Ser. Khim.* 759 (1989) [c]
34. M Breitenkamp, J Lilie, A Henglein *Ber. Bunsenges. Phys. Chem.* **80** 973 (1976)
35. N L Sukhov, B G Ershov *Khim. Vys. Energ.* **16** 511 (1982) [a]
36. A Fojtic, E Janata, A Henglein *J. Phys. Chem.* **96** 4734 (1992)
37. N L Sukhov, B G Ershov *Izv. Akad. Nauk SSSR, Ser. Khim.* 952 (1984) [c]
38. S Mosseri, A Henglein, E Janata *J. Phys. Chem.* **94** 2722 (1990)
39. N L Sukhov, B G Ershov *Izv. Akad. Nauk SSSR, Ser. Khim.* 716 (1984) [c]
40. N L Sukhov, B G Ershov *Khim. Vys. Energ.* **22** 409 (1986) [a]
41. B Ershov, M Akinshin, A Gordeev, N Sukhov *Radiat. Phys. Chem.* **27** 911 (1986)
42. B G Ershov, A K Pikaev *Res. Rev.* **1** 2 (1969)
43. B G Ershov, Doctoral Thesis in Chemical Sciences, Institute of Physical Chemistry of the Academy of Sciences of the USSR, 1972
44. P N Moorthy, J J Weiss *Adv. Chem.* **50** 180 (1965)
45. M C Schields, M C R Symons *Mol. Phys.* **19** 571 (1966)
46. R S Eashus, M C R Symons *J. Chem. Soc., A* 286 (1970)

47. R J Booth, H C Starkie, M C R Symons *J. Chem. Soc., A* 3198 (1971)
48. R J Booth, H C Starkie, M C R Symons *J. Chem. Soc., A* 2233 (1973)
49. A I Aleksandrov, B G Ershov, A K Pikaev, V I Spitsyn *Izv. Akad. Nauk SSSR, Ser. Khim.* 249 (1976) [c]
50. B G Ershov, A I Aleksandrov, V I Spitsyn *Dokl. Akad. Nauk SSSR* **229** 1120 (1976) [b]
51. B G Ershov, A I Aleksandrov, V I Spitsyn *Dokl. Akad. Nauk SSSR* **242** 1086 (1978) [b]
52. B G Ershov, A I Aleksandrov *Izv. Akad. Nauk SSSR, Ser. Khim.* 743 (1978) [c]
53. B G Ershov, A I Aleksandrov *Radiat. Phys. Chem.* **10** 327 (1979)
54. A I Aleksandrov, G V Ionova, B G Ershov *Radiat. Phys. Chem.* **13** 199 (1979)
55. A I Aleksandrov, B G Ershov, V I Spitsyn *Dokl. Akad. Nauk SSSR* **254** 907 (1980) [b]
56. B G Ershov, A I Aleksandrov, V I Spitsyn *Izv. Akad. Nauk SSSR, Ser. Khim.* 768 (1982) [c]
57. G Breit, I I Rabi *Phys. Rev.* **38** 2082 (1931)
58. R A Zhitnikov, N V Kolesnikov *Zh. Eksp. Teor. Fiz.* **46** 59 (1964)
59. B G Ershov, A I Aleksandrov *Teor. Eksp. Khim.* **14** 679 (1978) [d]
60. G Werth *Phys. Rev. Lett.* **30** 1155 (1973)
61. M F Crowford, A L Schawlow *Phys. Rev.* **79** 1310 (1949)
62. A L Schawlow, J N Hume, M F Crowford *Phys. Rev.* **79** 1876 (1940)
63. B G Ershov, N L Sukhov, G V Ionova, V I Spitsyn *Zh. Neorg. Khim.* **31** 1363 (1986) [e]
64. G V Ionova, B G Ershov, V I Spitsyn *Dokl. Akad. Nauk SSSR* **261**1400 (1986) [b]
65. C E Moore *Atomic Energy Levels* Vol. 3. (Washington, NBS USA, 1971)
66. A V Gogolev, I E Makarov, A K Pikaev *Khim. Vys Energ.* **15** 109 (1981) [a]
67. J H Baxendale, R S Dixon *Z. Phys. Chem.* **B43** 161 (1964)
68. W M Latimer *The Oxidation States of the Elements and their Potentials in Aqueous Solutions* (New York, 1952)
69. B F Johnson, R Davis, in *Comprehensive Inorganic Chemistry* Vol. 3 (New York: Pergamon Press, 1974) p. 132
70. A Busev, in *Analytical Chemistry of Indium* (Oxford: Pergamon Press, 1962) p. 28
71. G V Ionova *Radiokhimiya* **4** 457 (1982) [f]
72. B G Ershov, N L Sukhov *Izv. Akad. Nauk SSSR, Ser. Khim.* 1971 (1985) [c]
73. V A Nazarenko, V P Antonovich, E M Nevskaya, in *Gidroliz Ionov Metallov v Razbavlennykh Rastvorakh* (Hydrolysis of Metal Ions in Diluted Solutions) (Moscow: Atomizdat, 1979) p. 192
74. A A Grinberg *Vvedenie v Khimiyu Kompleksnykh Soedinenii* (Introduction to the Chemistry of Complex Compounds) (Moscow: Goskhimizdat, 1951) p. 21
75. F Basolo, R C Johnson *Coordination Chemistry* (New York: W A Benjamin Inc., 1964) p. 31
76. R W Dodson, H A Schwarz *J. Phys. Chem.* **78** 892 (1974)
77. A I Aleksandrov, A I Prokof'ev, N N Bubnov *Usp. Khim.* **65** 519 (1996) [*Russ. Chem. Rev.* **65** 479 (1996)]
78. N L Sukhov, B G Ershov *Khim. Vys. Energ.* **30** 171 (1996) [a]
79. B G Ershov, E Janata, A Henglein *J. Phys. Chem.* **98** 10891 (1994)
80. D A Troitskii, N L Sukhov, B G Ershov, A V Gordeev *Khim. Vys. Energ.* **28** 218 (1994) [a]
81. S Remita, M Mostafavi, M O Delcourt *New J. Chem.* **18** 581 (1994)
82. B G Ershov, E Janata, M Michaelis, A Henglein *J. Phys. Chem.* **95** 8996 (1991)
83. B G Ershov *Izv. Akad. Nauk, Ser. Khim.* 25 (1994) [c]
84. A Henglein, M Gutierrez, E Janata, B G Ershov *J. Phys. Chem.* **96** 4598 (1992)
85. D A Troitskii, N L Sukhov, B G Ershov *Khim. Vys. Energ.* **28** 221 (1994) [a]
86. B G Ershov, N L Sukhov, D A Troitskii *Zh. Fiz. Khim.* **68** 820 (1994) [g]
87. O Platzer, J Amblard, J L Marignier, J Belloni *J. Phys. Chem.* **96** 2334 (1992)
88. J Amblard, O Platzer, J Ridard, J Belloni *J. Phys. Chem.* **96** 2341 (1992)
89. S Kapoor, D Lowless, P Kennepohl, D Meisel, N Serpone *Langmuir* **10** 3018 (1994)
90. D Lowless, S Kapoor, P Kennepohl, D Meisel, N Serpone *J. Phys. Chem.* **98** 3018 (1994)
91. L N Lewis *Chem. Rev.* **93** 2693 (1993)
92. B C Gates *Chem. Rev.* **95** 511 (1995)
93. M R Hoffman, S T Martin, W Choi, D W Bahnemann *Chem. Rev.* **95** 69 (1995)

[a] — *High Energy Chem. (Engl. Transl.)*
[b] — *Dokl. Chem. (Engl. Transl.)*
[c] — *Russ. Chem. Bull.*
[d] — *Theor. Exp. Chem. (Engl. Transl.)*
[e] —*Russ. J. Inorg. Chem. (Engl. Transl.)*
[f] — *Russ. Radiochem. (Engl. Transl.)*
[g] — *Russ. J. Phys. Chem. (Engl. Transl.)*