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The problem of oxidation state stabilisation and some regularities of a Periodic system of the elements

Yu M Kiselev, Yu D Tretiyakov

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Abstract. The general principles of the concept of oxidation state stabilisation are formulated. Problems associated with the preparation and provision of the highest valent forms of transition elements are considered. The empirical data concerning the synthesis of new compounds of rare-earth elements and *d* elements in unusually high oxidation states are analysed. The possibility of occurrence of the oxidation states + 9 and + 10 for some elements (for example, for iridium and platinum in tetraoxo ions) are discussed. Approaches to the realisation of these states are outlined and it is demonstrated that solid phases or matrices containing alkali metal cations are the most promising systems for the stabilisation of these high oxidation states. Selected thermodynamic features typical of metal halides and oxides and the regularities of the changes in the extreme oxidation states of *d* elements are considered. The bibliography includes 266 references.

I. Introduction

According to traditional concepts, chemical compounds contain elements in definite oxidation states (OS). These concepts form the basis of, for example, authoritative handbooks on inorganic and coordination chemistry.[1,2] A hypothesis for the stabilisation of the oxidation states has been offered rather long ago. The theoretical and experimental aspects of this hypothesis were discussed in the early 1960s (see, for example, Refs 3 – 7). More recently, the experimental aspect of the problem of the existence and OS stabilisation was repeatedly considered in connection with the discovery of noble gas compounds,[8] studies of chemical properties of transactinides[9,10] and the preparation of compounds of Np^{VII}, Pu^{VII},[10] Am^{VII},[11–14] Cm^{VI},[15] Rn^{VI},[16] Cf^{V},[17] Cm^{V},[15,18] Au^{V},[19] Ag^{V},[20] Es^{IV},[18] Cu^{IV},[21] Tm^{IV}[22] and lanthanides and actinides in the lowest oxidation states.[23–29] Worthy of mention are investigations that have demonstrated the similarity of the properties of heavy actinides and lanthanides, the discovery of the specificity of the so-called tetrad effect in lanthanide compounds,[23,29,30] the preparation of Fe^{VIII} (see. Refs 31 and 32) and the detection of Co^{VI} in a cesium ferrate matrix.[33,34] Studies of the properties of elements with atomic numbers 104, 105 and 106, *viz*., rutherfordium, dubnium and seaborgium,[35,36] and the possibility of generation of Hg^{IV} (see Refs 37 and 38) are also worthy of note.

Recently, new aspects of the problem under consideration became apparent to researchers in connection with the development of novel techniques for the stabilisation of oxidation states. With this in mind, Yatsimirskii[39,40] and Parry[41] examined the OS stabilisation upon coordination based on the original data. Previously, we have considered different aspects of this problem. In particular, we have discussed the stability of the highest OS of lanthanides in fluoride systems,[29,42] the effect of outer-sphere cations on the stability of coordination compounds,[43] the ways of attaining high OS in the oxidative fluorination reactions,[44] procedures for the identification of the valent forms of transition elements[45] and some problems associated with the concept of valence,[46] in particular, some aspects of the problem of OS stabilisation in the solid phase[47] and the possibility of generation of high valent forms ($\geqslant +8$) of the heaviest transition elements (Ir, Pt, Au and Hg).[48] The validity of the principles reported in Ref. 48 was confirmed by direct quantum-chemical calculations.[49]

In the present review, we consider some problems of OS stabilisation in relation to new evidence on their stability and touch on the problem of the extreme valent possibilities of transition elements. The concept of 'oxidation state stabilisation' is useful in this discussion because it provides ideas and mechanisms which allow researchers not only to perform experimental studies but also to interpret the results obtained. Let us formulate the general principles of this concept.

II. A concept of oxidation state stabilisation

It is generally assumed that chemical compounds contain elements in certain OS, which are stabilised by various forces. The character of chemical processes which result in a change in the oxidation state depends on the properties of the ion to be stabilised and the corresponding coordination environment.[7,50,51] In the studies of OS stabilisation, the possibility of formation of compounds of a particular element in the particular OS and their stability are determined and the conditions for the synthesis of these com-

Yu M Kiselev, Yu D Tretiyakov Department of Chemistry, M V Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russian Federation. Fax (7-095) 932 88 46. Tel. (7-095) 939 22 52. E-mail: kiselev@coord.chem.msu.ru (Yu M Kiselev) Tel. (7-095) 939 20 74 (Yu D Tretiyakov)

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pounds are searched for, *i.e.*, techniques and procedures for the preparation of compounds with the predetermined property, *viz.*, OS, are developed and factors that affect the stability of OS are revealed (for example, phenomenologically).

Quite apparently, it is impossible to reveal the stabilisation factors without considering the problem of stabilisation of coordination polyhedra and crystalline phases. The strength of the corresponding chemical bonds and the stability of OS can be enhanced by stabilising coordination polyhedra.[52–56]

Within the framework of the concept under consideration, it is assumed that the OS stabilisation implies an increase in the lifetime of the oxidised (reduced) form in an oxidant–reductant dynamic system compared to the standard. This system is characterised by certain thermodynamic and kinetic parameters (for example, by the Gibbs potential, vapour pressure, the activation energy, the reaction order, *etc.*). To stabilise OS, one can vary these parameters or change the 'thermodynamics' and/or 'kinetics' for those that are more favourable for the increase in the lifetime of the oxidised (reduced) form.

Let us consider the following transformation:

$$Pr^{III}_{aq} \rightleftharpoons Pr^{IV}_{aq} + e^{-}_{aq}. \quad (1)$$

The Pr^{IV}_{aq} aqua ion exists in aqueous media for ~ 200 ns,[57,58] whereupon this ion is transformed into the Pr^{III}_{aq} aqua ion. When phosphotungstic acid is introduced into this dynamic system, a Pr^{IV} heteropolycompound [containing an ion of the probable composition $Pr^{IV}W_{12}O^{5-}_{40}$ (see Ref. 59)] is formed and the lifetime of the 'oxidised' form containing Pr^{IV} is increased to 10–15 min. Consequently, a change in the coordination environment about the Pr^{IV} ion is accompanied by a change in its stability. We do not consider the kinetic characteristics of redox processes in the absence and in the presence of heteropolyacids. However, it is evident that a change in the nearest environment of the central ion in the complex is reflected in the kinetic parameters.

The problem of stabilisation has two aspects. The first aspect is associated with the ways of attaining the desired oxidation state. The second aspect concerns the stability of this state. It is the provision of the stability of the OS over a period of time which is sufficient for its formation, identification and utilisation of the properties that receives primary attention.

The stability of chemical compounds with respect to decomposition into elements is determined by the total energy of the ligand–central atom system:

$$E_{tot} = \sum E_i + E' + E'' + E_c, \quad (2)$$

where E_i is the bond energy of the ith molecular orbital of the isolated complex formed upon interaction of the electron system of the central atom with the ligand, E' is the energy of stabilisation due to loss of degeneracy, E'' is the energy of repulsion between the ligands and E_c is the energy of stabilisation due to establishment of the long-range order (crystal lattice).[51]

Analysis of Eqn (2) demonstrates that the stability of compounds is governed by a combination of properties of the central atom and the ligand environment as well as by the crystal structure. Many researchers have reached this conclusion in an empirical consideration of the problem (see, for example, Refs 4 and 5).

The factors that affect the stability of OS are diverse in nature and generally act simultaneously and competitively.[5] However, these factors can be, though rather arbitrarily, divided into thermodynamic (the first group) and kinetic (the second group) factors. The factors of the first group determine the possibility of formation of a particular ligand environment about the central atom (the formation of the short-range or long-range order). The factors of the second group affect the rate of formation of the desired environment. Taking into account the aforesaid, the following ways of stabilising OS can be distinguished.

1. Stabilisation through coordination. This stabilisation is realised in the chemical process owing to the formation of the nearest environment of the central atom in the complex, which is more stable than those in free ions in the gaseous state or in solvated ions in solution. In this case, the ligands, the geometry, *etc.* are selected.[7]

2. Stabilisation by the crystal lattice, which is realised due to an increase in the coordination saturation of the central atom in the course of formation of crystals compared to the coordination saturation of ions in the gaseous state or in solution.[7,47]

3. Kinetic stabilisation due to minimisation of kinetic barriers that appear in the course of formation of the thermodynamically more favourable nearest environment of the central atom.[7]

A particular technique for the stabilisation should be chosen taking into account the properties of both the reagents and the expected reaction products containing the ion (atom) to be stabilised. Thus, the stability of compounds in which the coordination polyhedron about the 'highly oxidised central atom' is formed from the most stable F^- and O^{2-} ions, which are the strongest, difficultly oxidisable and difficultly deformable, are generally a maximum. Probably, only these ligands in the nearest coordination sphere of the central atom are suitable for stabilisation of the high and the highest unstable OS. Therefore, compounds with oxide and fluoride coordination polyhedra are generally considered in studies on the stabilisation of the highest OS.

Direct and inverse problems can be distinguished in the analysis of problems associated with the stability of valent forms.

The problem is said to be direct if physicochemical characteristics of an oxidant–reductant system, for example, redox potentials, are determined experimentally or calculated. The problem is said to be inverse if the conclusion about the stability of the oxidation state is made from a change in the selected parameters (properties) which can be related to OS in some series of compounds.

These problems can in principle be solved because rather simple correlations exist between the energy characteristics of the ions to which particular valent forms are assigned.

Actually, the quantum-mechanical parameters which characterise the electron density distribution and which are calculated taking into account only the electrostatic interactions between nuclei and electrons (the first-order perturbation theory) directly correlate with the oxidation states of the elements. This can be exemplified by the linear equation for the chemical shifts in the Mössbauer spectra (Fig. 1).[32,60,61]

$$\delta = a + bx,$$

where δ is the chemical shift, $a = 1.834$, $b = -0.456$ and x is OS.

There are rather simple correlations between the enthalpies of formation of halides $MHal_n$ and the enthalpy increments of M^{n+} ions calculated according to the additive schemes.[62] These correlations can be interpreted in a different way (see, for example, Ref. 63) because of the ambiguity of the approaches used by chemists or, more precisely, due to the fact that none of approaches can be extended indiscriminately to all compounds.

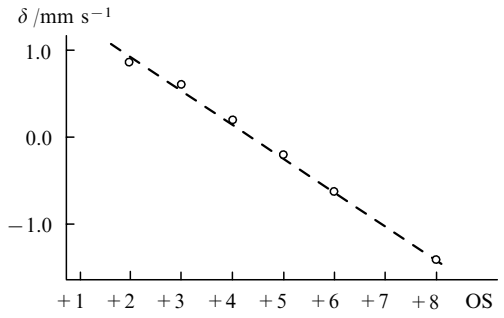


Figure 1. Dependence of the chemical shift relative to sodium nitroprusside on OS of the metal for iron derivatives.[32,60,61]

In the general case, the direct and inverse problems cannot be solved. This is associated with many factors but the main reason is that M_{aq}^{n+} aqua ions that exist in solutions are known only for a limited number of elements (generally, in the lowest OS). As the atomic number of the element is increased, the covalence of the M–L bond and the role of relativistic effects, including spin-orbital interactions, are increased, which is accompanied by the enhancement of the characteristic features of the ions more complex than aqua ions (for example, of actinyl ions [64]). An analogous situation is observed as the OS is increased.

The definition of the notion 'oxidation state' is the key in the analysis of the problems associated with the concept under consideration. This problem, which is directly related to the 'problem of valence,' is intricate. In particular, the problem of the relationship between the valence number, the effective charge and OS is still topical, although it has been discussed many times. This aspect of the chemical structure theory turned to be so contradictory that it has been suggested,[65] without going into terminological details, to consider the valence only as a number, to retain its classical content and to give up attempting to treat all modern discoveries in the field of chemical bonds in the context of this notion. However, more recently (see, for example, Refs 66 and 67) attempts to calculate the valence numbers have been undertaken. No consideration is given to these and other calculation procedures in the present discussion, but it should be noted that none of the available procedures is versatile.

The measure of the valence or OS can be most readily determined by the number of gram-equivalents of the oxidising or reducing agent per gram-atom of the element (metal or metalloid) which is either consumed or acquired when the element is transformed to the compound or vice versa. It is advantageous to take a one-equivalent oxidation or reduction process as the standard process, the choice of a particular one-equivalent conversion being of no importance. The above-described determination of the valence number † is convenient because it is based on experimental grounds and is invariant with respect to the model of the electronic structure of the compound.

We emphasise that the positive or negative value of OS does not imply that the corresponding charge is located on the atom. The determination of the valence on the basis of the number of gram-equivalents means the thermodynamic relations from which neither the spatial arrangement of the atoms nor characteristics of the bonds (for example, the bond order, which cannot be determined spectroscopically) can be directly obtained. The gram-equivalent is a complex parameter, which covers all interactions in the compound, and it cannot be represented either as a charge or as a number of bonds.

The valence (or OS) is a classification notion used in crystal chemistry or for systematising educational data on inorganic chemistry. For example, Kossel's views were consistently used in the monograph [69] for tetrahedral systems. Chemical compounds of the element in the same oxidation state can be characterised by different electron density distributions, coordination polyhedra and the bond character. This is not surprising because specific electronic properties of atoms, which can be judged from the results of physical methods, are nothing more than a consequence of the manifestation of a particular valence. The above-considered determination of the valence number does not contradict the notions [71] of the electronic state fluctuation, processes of electronic ordering and, consequently, fractional OS for transition elements. These are the properties of the element which exists in a particular OS or possesses a definite valence. These properties should be specially studied and systematised.

The results of calculations of the enthalpies of formation of inorganic halides and oxides according to additive schemes provide certain support for the above approach to the determination of the valence.[62, 72–75]

Calculations of the enthalpies (energies) of inorganic halides and oxides are based on the classical structure theory, which has been conceptually refined by Tatevskii.[76, 77] According to the known approximation of this theory, the macrocharacteristic, such as the self-energy, can be represented as a sum of increments (E_j) that characterise contributions of the so-called effective jth atoms with the valence number (n), $j^{(n)}$:

$$\Delta U = \sum E_{j^{(n)}}. \tag{3}$$

The application of this equation to inorganic subjects is limited. Equation (3) cannot be directly used even in the seemingly simple case, *viz*., in the case of compounds of various metals of the same stoichiometry, because one has to solve a system of k equations of the type

$$\Delta U_{A_xB_y} = x E_{A^{(n)}} + y E_B \ [E_A = \Phi(n), E_B = \text{const}] \tag{4}$$

in $k + 1$ unknowns. One more equation is required to obtain a solution. We found an equation of relationship,[62, 73, 78] which is an empirical correlation between the enthalpy of formation of compounds MXn and the enthalpy of the following type:

$$H_{M^{(n)}} \equiv \frac{\sum I_i}{I_1} \Delta_s H_M,$$

where I_i are stepwise ionisation potentials and $\Delta_s H_M$ is the enthalpy of sublimation of the metal.

The equation takes the form of the following additive four-membered equation:

$$\Delta_f H^\circ_{MX_n} = H_{M^{(n)}} + nH_X + nH_{M^{(n)}-X} + yH_{X-X}, \tag{5}$$

where $H_{M^{(n)}}$ is the enthalpy corresponding to the contribution of the central atom, H_X, $H_{M^{(n)}-X}$ and H_{X-X} are the enthalpies corresponding to the contributions of the ligand X and of the $M^{(n)}$–X and X–X bonds, respectively. Examples of selected dependences of the enthalpies of formation of chlorides and fluorides on the first term of Eqn (5) are given on Fig. 2 and in Table 1.

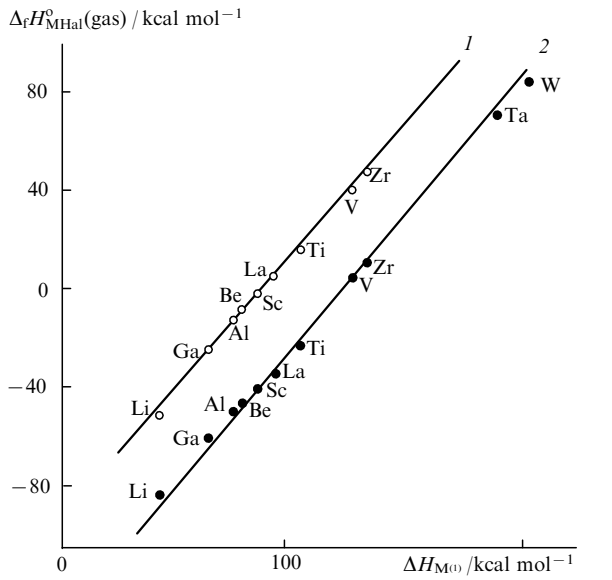


Figure 2. Dependence of the enthalpy of formation of gaseous monohalides on the partial enthalpy $H_{M^{(1)}}$; (*1*) chlorides; (*2*) fluorides.

† In this approach, the valence numbers coincide with the so-called Jorgensen's formal OS (or the Russian term 'degrees of oxidation'). The application of the latter is improper because of the absence of charges on atoms. Crystal-chemists use 'formal charges' on atoms in calculations [68, 69] and reject the reality of these charges by introducing the notion 'effective charges.' The valence balance or valence strengths would be more properly used (this approach was used, for example, in Ref. 70).

Table 1. Coefficients of the linear dependence $\Delta_f H^\circ = A + BH_{M^{(n)}}$ for gaseous metal halides.

Halide	Metal	*A*	*B*
MF	**Na**, **K**, **Rb**, **Cs**, Ag, Tl	−112.7	1.636
	Li, Be, Al, Sc, Ti, V, Ga, Zr, Ta, La–Lu	−117.4	0.970
	Ca, Sr, Ba, Cr, Mn, Fe, Co, Ni, Cu, In	−126.3	1.479
	Zn, Cd, Hg, Sn, Pb, Zr, Hf, Y	−26.0	0
MF_2	**Mg**, **Ba**, **Ra**, **Zn**, **Cd**, **Hg**, Yb	115.0	−1.930
	Be, Cr, Mn, Fe, Co, Ni, Ga, Mo, Tc, Ru, Rh, Pd, Ag, In, Sn, Ta, W, Re, Os, Ir, Pt	−193.6	0.328
	Sn, Pb, Zr, Hf	−89.9	−0.0999
	Sr, Sc, La–Lu	−217.9	0.252
	Cu, Zn, Pb, Ru, Rh, Pd, Os, Ir, Pt	−141.8	0.252
	Al, Ti, V, Ga, Y, Nb, Mo, Tc, La, Ta, W	−340.1	0.486
MF_3	**Al**, **Ga**, **In**, **Tl**, Mn	−44.1	−0.280
	Al, Ti, Zr	−345.5	0.0841
	Sc, Y, La– Lu	−302.7	0
MCl	**Na**, **K**, **Rb**, **Cs**, Ag, Tl, Mg, Ca, Sr, Ba	−87.1	1.636
	Li, Al, Be, Sc, Ti, V, Ga, Zr, Ta, La–Lu	−84.9	0.970
	Cr, Mn, Fe, Co, Ni, Cu, In, Sn	−100.3	1.479
	Zn, Cd, Hg, Sn, Pb, Zr, Hf, Y	5.0	0
MCl_2	**Mg**, **Ba**, **Ra**, **Zn**, **Cd**, Yb	105.1	−1.930
	Cr, Mn, Fe, Co, Ni, Mo, Tc, Ru, Rh, Pd, Ag, In, Re, Os, Ir, Pt, Au, Tm	−129.5	0.328
	Sn, Pb, Hf, Hg	−26.0	−0.0999
	Be, Al, Sc, Ti, V, Ga, Y, Ca, Sr, Ba, Zr, Nb, Mo, Tc, Ru, Ag, La, Hf, Ta, W, Re, Ce–Lu	−144.4	0.252
	Cu, Zn, Rh, Pd, Os, Ir, Pt, Pb	−77.3	0.252
MCl_3	**Al**, **Ga**, **In**, **Tl**	57.8	−0.280
	Cr, Mn, Fe, Ir	−233.6	0.239
	Sc, Y, La–Lu	−170.2	0

Note. The characteristic groups, *i.e*., the sets of compounds of elements of the corresponding vertical groups in the short version of the Periodic system, are given in boldface type.

$$\Delta_f H^\circ = A + BH_{M^{(n)}}.$$

A similar situation is also observed for other halides and oxides.

The so-called characteristic sets of compounds can be distinguished in these linear dependences. The Group I elements are characteristic for monohalides (see Fig. 2), the Group II elements are characteristic for dihalides, *etc*. In other words, the characteristic sets of compounds of elements with the *i*th valence are comparable with the lists of the elements in the vertical groups of the short version of the Periodic system.

Taking into account the additive equation (5) and the linear dependences of the enthalpies of formation of gaseous halides on the enthalpies $H_{M^{(n)}}$, it can be concluded that grouping of compounds is dictated by the argument, while the character of the change in the function is determined by the remaining terms of the additive sum in Eqn (5).

The relationship between the enthalpy increments is such that the first terms of the sum (5) have the maximum values. This makes it possible to construct the hierarchy which defines the energetics of compounds and which is based on the classical structure theory.[76,77]

This theory assumes the application of the model of pairwise interactions. A certain energy increment can be related to each pairwise interaction (the procedure is described in the monograph [76]). The values of the increments depend on the following characteristics: chemical individuality, sort, type, kind and variety. On the whole, these characteristics comprise a 'tree' of chemical states. The first characteristic is determined by the position of the element in the Periodic system. The second characteristic is associated with the valence. The third characteristic is connected with the geometry of the nearest environment of the central atom. The last two mentioned characteristics reflect finer details of the structure, for example, geometrical or optical isomerism.

The characteristics of the sort (valence), which determine, in particular, clustering of halides (or oxides) in the dependences analogous to those shown in Fig. 2, can be assigned to the parameter $H_{M^{(n)}}$. As a consequence, the valence is determined through the gram-equivalent, *i.e*., through the thermodynamic relations.

The oxidation states can be determined by direct (chemical) and indirect (physical) methods. Oxidimetric and electrochemical techniques were referred to as the chemical methods in Ref. 45. Procedures for the analysis based on one-equivalent transitions of the types $I^- \rightarrow (1/2)I_2$ and $Ce^{III} \rightarrow Ce^{IV}$ as well as on processes described by a known number of equivalents ($MnO_4^- \rightarrow Mn^{II}$ and $Cr_2O_7^{2-} \rightarrow Cr^{III}$) are very popular. Of the above-mentioned procedures, iodometric techniques are most widely used because of their simplicity, availability and versatility.

For example, the applications of the iodometric analysis to fluoride-containing oxidants, which include compounds of *d* and *f* transition elements, and to platinum compounds were considered.[79,80] Fluorides of Ln^{IV}, Cu^{II}, Cu^{III}, Ag^{II}, Ag^{III}, Ag^{V}, Au^{V}, Ni^{III}, Ni^{IV}, Mn^{III}, Mn^{IV}, Co^{III}, Fe^{III}, Fe^{IV}, Cl^{III}, Br^{III}, Br^{V}, Xe^{II}, Xe^{IV}, Xe^{VI}, *etc*. were analysed. The iodometric procedure was used in the analysis of alkaline solutions of iron derivatives in the highest oxidation states (Fe^{IV}, Fe^{VI} and Fe^{VIII}).[81] In this case, not only the OS of iron but also the concentration of the metal in solution was determined.

The determination of the final state after titration is the key to oxidimetric (in particular, iodometric) procedures. Thus experiments with platinum compounds demonstrated [80] that $Pt^{2.3+}$ was the final state in the titration of iodide complexes, which does not prevent the analysis.

Evidently, the main drawback of oxidimetric procedures is the absence of selectivity. This calls for studies aimed at revealing reasons for redox transformations. For example, the analysis of alkaline solutions of iron in the highest oxidation state was accompanied by additional studies of solutions by Mössbauer spectroscopy, which have demonstrated that the iodometric data correspond to the valence transitions of iron.[81]

Much the same is true for electrochemical methods, *viz*., for polarography and coulometry. Cyclic voltammetry in combination with coulometry is a convenient procedure for the determination of gram-equivalents in metal complexes.[82] For example, two reversible one-electron waves corresponding to the $Ir^{VI} \rightarrow Ir^{V} \rightarrow Ir^{IV}$ transformations are observed in the cyclic voltammograms of reduction of the electrochemically oxidised hydroxo complexes of Ir^{IV}.[83,84] Electrochemical methods can be applied not only to solutions but also to melts. For example, these procedures were used for revealing the nature of the processes in salt melts and for determining conditions for stabilisation of the highest transition-element OS in these melts.[85]

Chemical methods for the OS determination are effective only in combination with physical methods. The most commonly used methods are magnetochemistry, ESR, electronic, Mössbauer and X-ray spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction analysis and methods of vibrational spectroscopy.[45] To answer the question about the element OS, it is necessary to know, first, the correlations between OS and the parameter observed and, second, the reasons for deviations from these correlations if these deviations are observed or expected. For example, the number of outer electrons withdrawn from the electronic configuration of the free atom often corresponds to the element OS. In addition, the number of gram-equivalents of the oxidising (reducing) agent consumed in the oxidimetric titration corresponds to the number of *d* (or *f*) electrons of the metal ion (for a series of important regularities, see Refs 86–88).

Below are considered procedures for the stabilisation of the highest OS of particular elements.

III. Rare-earth elements

The known OS [89, 90] for rare-earth elements (REE, Ln) are listed in Table 2. For rare-earth elements, OS +3 is generally realised in a rich variety of their compounds; OS +2 belongs to the lowest OS and is not considered in the present paper because many studies were devoted to this problem and the results have been reviewed.[23]

Table 2. Known oxidation states of rare-earth elements.[89, 90]

OS	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
+2	?	?	+	+	?	+	+	?	?	+	+	+	+	+	?
+3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
+4		+	+	+		+			+	+			+		

Note. Hereinafter, the following notations are used: +, this OS exists; ?, indirect evidence is available and reliable proof is absent.

1. Complexes of Ln^{IV} with organic ligands

The problem of preparation of rare-earth complexes in high OS with organic ligands arose in the 20th century.[91–93] These compounds are often characterised by high stability constants and are very promising, for example, for the separation of rare-earth elements and actinides.[94–96] In the 1970s, it was established that intramolecular redox processes cannot be completely eliminated even in Ce^{IV} compounds (see, for example, Ref. 97), and the number of studies aimed at this particular application became fewer. However, it was reported [98] that the influence of these processes in rare-earth complexes with diphthalocyanines was a minimum, and it was concluded that these subjects contain Ln^{IV} ions throughout the entire lanthanide family. Nevertheless, a number of facts do not allow one to accept this interpretation of the data made in the work cited. In studies of transition metal complexes in the highest OS with carboxyl-containing chelating agents, hydroxy carboxylic acids, polydentate acyclic ligands, crown ethers and β-diketones, it was demonstrated that redox processes occur in all cases, though at different rates.[97] In other words, intramolecular redox interactions can only be partially suppressed (but not completely excluded) by choosing an appropriate ligand. Phthalocyanine can be readily reduced due to the presence of a large number of multiple bonds. Even if rare-earth complexes under consideration possess high stability, one cannot expect that intramolecular redox processes would be completely suppressed taking into account extremely high values of the redox potentials of the Ln^{III}/Ln^{IV} pairs (for example, the values of E° were estimated as equal to 2.83.0 V for Ln = Tb and Pr [99, 100]). Apparently, additional supporting evidence for the existence of Ln^{IV} in diphthalocyanines is required.[101]

2. Complexes of Ln^{IV} with inorganic ligands

The data on the behaviour of Ln^{IV} (Ln = Ce, Pr, Nd, Tb and Dy) in aqueous media are limited mainly by those for Ce^{IV} compounds. The Ce^{IV} ion is a rather strong oxidant ($E^\circ_{Ce^{IV}/Ce^{III}}$ = 1.66 V [99, 100]). These ions are formed in the reactions with the participation of oxidants such as bromate (see, for example, Ref. 102) and are stabilised by various inorganic ligands with different efficiency. Interestingly, Ce^{IV} compounds containing chloride ions in the nearest coordination sphere exist although Cl^- ions are known as reductants. For example, a large series of hexachlorocerates(IV) $M^I_2Ce^{IV}Cl_6$ ($M^I = NR_4^+$, PR_4^+, AsR_4^+, H_3O^+, Rb^+ and Cs^+) were prepared and their structures and stabilities were studied.[103–112] It was demonstrated [113] that the anionic $[CeCl_6^{2-}]$ complex exists in aqueous media for a rather long period of time and an excess of chloride ions even somewhat stabilises this complex. The cesium salt (air-stable below 300 °C) is a convenient gravimetric form in the chemical analysis and separation of alkali metal cations.[105]

Data on the existence of Tb^{IV} and Pr^{IV} in aqueous media are scarce. Note that the information on the preparation of Pr^{IV} and Tb^{IV} acido complexes (nitrates, sulfates and chlorides) in aqueous solution was disproved.[114] As mentioned above, reliable data on the Pr^{IV} ions were obtained by pulse radiolysis:[57, 58] the short-lived absorption was assigned to the Pr^{IV} aqua ion. The Pr^{IV} ion is unstable due to the larger value of the Pr^{IV}/Pr^{III} pair redox potential. The preparation of aqueous solutions of Pr^{IV} phosphotungstate was reported.[115–117] The possibilities of studying this deep coloured complex are limited since this complex exists in a solution for only several minutes even at low concentrations. As a consequence, detailed information on this complex is absent.

Tetravalent terbium ($E^\circ_{Tb^{IV}/Tb^{III}} \simeq 2.8$ V) is also stabilised in a salt of phosphotungstic acid.[59, 117, 118] Its solutions can be stored at room temperature for several months. Phosphotungstic acid can be very efficiently used for stabilising strong oxidants, such as actinide ions, and the complexation leads to a decrease in the E° value by $\sim$ 1.0 V.[118, 119] The evidence on the existence of Pr^{IV} and Tb^{IV} ions in these compounds suggests that the above conclusion is true for lanthanides as well.

While on the subject of aqueous media, Pr^{IV} and Tb^{IV} hydroxides should be mentioned. Treatment of alkaline suspensions of Tb^{III} hydroxide with such reagents as O_3, $S_2O_8^{2-}$ and IO_4^- is accompanied by the formation of Tb^{IV} hydroxide.[120] Treatment of binary and complex Pr^{IV} and Tb^{IV} fluorides with alkaline solutions also resulted in the isolation of hydroxides.[121] Note that the yield of Ln^{IV} hydroxide decreases as the stability of Ln^{IV} ions decreases. Thus when the corresponding fluoride complex was treated with cold alkali, $Tb^{IV}O_2 \cdot nH_2O$ was obtained in almost quantitative yield, the yield in the case of Pr^{IV} was substantially lower and Dy^{IV} hydroxide was formed only in trace amounts.[121]

To summarise, the stabilisation of Ln^{IV} in solutions is insufficiently efficient due to a limited number of inorganic ligands which are able to decrease the redox potential of the system to a reasonable value. The stability of Ln^{IV} is substantially higher in the solid state than in solutions, which is manifested not only in the higher thermal stability of the solid compounds compared to that of the complexes in solutions but also in the broad assortment of the corresponding tetravalent ions [89, 122, 123] that occur in solid phases.

Solid fluoride complexes of Ce^{IV}, Tb^{IV}, Pr^{IV}, Nd^{IV}, Dy^{IV}, Tm^{IV} and Sm^{IV} (the data on the last two mentioned complexes were reported in Refs 22 and 29) and binary Ce^{IV}, Tb^{IV} and Pr^{IV} fluorides (the synthesis of pure PrF_4 was described for the first time in Refs 124 and 125) have been prepared to date. Binary oxides PrO_{2-x} and TbO_{2-x} ($x < 0.5$) and complex compounds were detected in oxygen-containing systems.[126, 127] A large number of Ln^{IV} ions (Pr^{IV}, Tb^{IV}, Nd^{IV} and Dy^{IV}) are stabilised in $BaCeO_3$,[128–130] which serves as a matrix. Stabilisation was performed under an atmosphere of oxygen at 1200–1400 °C.[128, 129, 131]

Therefore, the stability of a metal–ligand system in the solid phase (*i.e.*, in the presence of long-range order) is higher than that of this system in solution. The coordination effects that occur in the solid state diminish the intermolecular metal–ligand distances in the nearest coordination sphere about the central atom of the complex compared to the internuclear distances in the binary compounds,[132] which also favours the stabilisation of the Ln^{IV} ions.

The currently available evidence allows one to consider the regularities of stabilisation of the highest OS of lanthanides. Analysis of the stability of Ln^{IV} compounds based on the published data [29, 43, 133–137] allowed conclusions [29, 137] that the efficiency of Ln^{IV} stabilisation can be judged from only two groups of data. The first group includes the data on redox potentials or ionisation potentials of lanthanide atoms. However, this information does not allow reliable conclusions about the stability of Ln^{IV} because $E^\circ_{Ln^{IV}/Ln^{III}}$ are calculated by empirical methods and only the data on Ce^{IV} derivatives provide trustworthy basis for these calculations. The experimental E° values

for other Ln^{IV}/Ln^{III} pairs cannot be obtained due to the high oxidising capacity of Ln^{IV}, which does not allow one to construct an equilibrium electrochemical cell. The solution of the direct problem of the stability presents difficulties because the initial data are scarce. The series of the relative stabilities of oxidation states [122, 123] obtained on the above basis reflect only roughly the actual situation. Therefore, an alternative method which consists in the solution of the above-mentioned inverse problem is used for obtaining data on the stability of Ln^{IV}.

The thermodynamic characteristics of Ln^{IV} fluorides with composition Cs_3LnF_7 were reported.[135] The thermal stabilities of the same fluorides were also studied by methods of non-isothermal kinetics. The thermodynamic values were determined according to procedures of differential thermal analysis,[138] which have been developed and tested in special experiments, with the use of a specially designed sealed nickel cell whose sensitivity is close to that of the cell of a differential scanning calorimeter.[139–141] These procedures make it possible to obtain data on the enthalpies of fluorination reactions.

The most reliable values of the enthalpies and Gibbs energies of the reactions

$$M_3Ln^{IV}F_7 \longrightarrow M_3Ln^{III}F_6 + \tfrac{1}{2}F_2 \qquad (6)$$

for all rare-earth elements (Table 3) can be obtained on the basis of the available data [135–137] and results of calculations of the Born–Haber cycle.[135, 142–144]

Table 3. Results of calculations of the enthalpies of process (6) (kJ mol^{-1}) according to the Born–Haber cycle.[135]

Ln	ΔU	$-\Delta_r H^\circ$	Ln	ΔU	$-\Delta_r H^\circ$
Ce	3608	331	Tb	3809	239
Pr	3656	164	Dy	3827	95
Nd	3730	90	Ho	3852	22
Sm	3753	31	Er	3904	58
Eu	3774	−68	Tm	3986	136
Gd	3793	−184	Yb	3998	47

It was confirmed [135, 142–144] that in the LnF_4 series the cerium compound is the most stable one, this is followed by the terbium and praseodymium derivatives in order of decreasing stability. The thermal stability of the M_3LnF_7 complexes decreases in the following order: Ce > Tb > Pr > Dy.[137, 145, 146]

The thermodynamic stability of the complexes with respect to elimination of fluorine according to reaction (6) decreases on going from Ce to Sm: Ce > Tb > Pr > Dy > Tm > Nd > Sm. The stability of the highest OS (+4) of lanthanides decreases in the same order.

The regularity which is observed in the lanthanide series and is referred to as the 'tetrad effect' has been refined.[29, 137] In the series of the rare-earth elements, 'nodal points' exist in which the probability of changes in the composition, structure, the type of phase diagram and some other parameters is a maximum. The lanthanide family is divided into four segments (from whence the name 'tetrad' follows). This effect is most pronounced in the middle of the 4*f* series, which corresponds to the 'gadolinium break.'[29, 147, 148] This effect is most clearly manifested in the atomic properties (ionisation potentials, electron affinity, Gibbs energy, enthalpies of gaseous ions, *etc*.). The tetrad effect was attributed to the specific change in the electrostatic term of the exchange interaction of the *f* electrons in the Ln series.[145]

The thermodynamic data (ΔH° and ΔG°) for Ln^{IV} fluorides reproduce the tetrad effect.[29, 135] However, the distinguishing feature is that this effect is of different importance for the middle elements of each half of the series. This effect is more pronounced in the middle of the second half of the series. As a consequence, the stability of Tm^{IV} is anomalously high compared to that of Sm^{IV} due to the effect of the condensed state.

Actually,[137, 149] the difference between the lattice energies of $Ln^{III}F_3$ and $Ln^{IV}F_4$ or of $M_3Ln^{IV}F_7$ and $M_3Ln^{III}F_6$ (ΔU) and the differences between the corresponding enthalpies of formation (ΔH°) are related to the fourth ionisation potentials of the lanthanide atoms (I_4) by the following equation:

$$\Delta H^\circ + \Delta U + \text{const} = I_4.$$

The ΔU values in the lanthanide series change 'smoothly' (see Table 3) so that these values for the second half of the 4*f* series are substantially larger than those for the first one. Since the dependence of I_4 on the atomic number of the element is nonlinear and is governed by the tetrad effect, the $\Delta H^\circ(\Delta G^\circ)$ values should be changed analogously. This implies that the enthalpies (Gibbs energies) of formations of Tm^{IV} compounds should be larger in magnitude than the corresponding values for the Sm^{IV} compounds.

3. The effect of complexation

A large number of tetravalent rare-earth elements are stabilised in cesium fluoro complexes. The higher stability of the complexes compared to the corresponding binary compounds has been discussed many times (see, for example, Refs 29 and 42). In the solid phase, the stabilisation occurs due to the positive charge of the outer-sphere cation, which compensates for the negative charges on the complex anions.[43] The absence of the outer-sphere cations in the structure of a compound leads to a distortion of the coordination polyhedron of the central atom as a result of which the overall atomic system is destabilised. For example, the structure of AuF_5 is built of octahedra linked to each other and twisted into a helix.[150] In Au^V complex fluorides, there is no need for such twist and the anion has an octahedral shape.[151]

4. Valence possibilities of lanthanides

Efforts were made to extend the series of lanthanides which could be transformed into the highest OS and to reveal the possibilities of attaining OS higher than +4 by experimental methods.[121, 124, 137, 140, 141]

In the solution of the first problem, reactions were found which are characterised by minimal kinetic barriers to processes of formation and the maximum possibility of the $Ln^{III} \rightarrow Ln^{IV}$ transformation.[44] The reaction that proceeds according to the following general equation:

$$Cs_3LnCl_6 + 3.5\,XeF_2 \longrightarrow Cs_3LnF_7 + 3.5\,Xe + 3\,Cl_2.$$

is most suitable.

This reaction was successfully used for the preparation of Cs_3TmF_7; Tm^{IV} was identified by physicochemical methods. Experimental evidence (the data from differential thermal analysis) for the existence of Sm^{IV} was obtained.[44]

The solution of the second problem was considered using praseodymium, which exhibits the most promise for preparing the highest valent forms, as an example.[137] Various high- and low-temperature fluorination reactions of binary and complex chlorides, fluorides, nitrates and sulfates under diverse reaction conditions (with variations of the temperature and the duration of the reaction, in the presence or in the absence of a solvent, *etc*.) were studied. The most powerful oxidants, including fluorine, krypton difluoride, *etc*., were used. It appeared that in all cases fluorination afforded only Pr^{IV} compounds. Taking into account this fact and based on the theoretical grounds, it was concluded [29, 137] that +4 is the extreme OS for 4*f* elements due to strong localisation of 4*f* states in the atomic core of lanthanides and the presence of serious energy hindrances to the subsequent ionisation. These 4*f* elements differ sharply from 5*f* elements.

In conclusion, is should be noted that OS +4 for the rare-earth elements are also stabilised in other solid systems, in particular, in perovskites $BaTbO_3$, $SrCeO_3$,[152] $Ba_{1-y}Sr_yPrO_3$, $BaCe_yPr_{1-y}O_3$ and $Sr_yBa_{1-y}PrO_3$,[153] oxide superconductors

$Pb_2Sr_2Ce_{1-x}Ca_xCu_3O_8$[154] and $Pb_2Sr_2RCu_3O_8$ (R = Ce, Pr, Tb or Am[155]) and manganites $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{7+\delta}$,[156] $Pr_{1-x}(Ca,Sr)_xMnO_3$,[157] $Pr_{0.6}Ca_{0.4}MnO_3$[158] and $Pr_{0.6}(Ca,Sr)_{0.4}.MnO_3$.[159]

IV. Transition elements

Of all transition metals, the Group VIII elements, silver, gold and mercury are of most interest because researchers faced serious problems when preparing their highest valent forms.

1. Highest valent forms of iron

Until recently, it was assumed that the maximum valence of iron is no higher than +6 and this fact was even substantiated theoretically. Quantum-chemical calculations for Fe, Ru and Os tetroxides[160] demonstrated that FeO_4 is characterised by high populations of the atomic states, which excludes the formation of strong Fe–O bonds. However, this fact does not necessarily indicate that this compound, though unstable, cannot be prepared. For iron, an OS of +5 was observed only in one compound, *viz*., in La_2LiFeO_6, which was prepared at high pressure and was well studied.[161] The seemingly well-known ferrates(VI) continue to attract the attention of researchers. For example, the mechanism of decomposition of ferrate(VI) was considered in Ref. 162. At the same time, Fe^{IV} compounds remain poorly studied.

The processes that occur in alkaline media upon anodic dissolution of metallic iron under conditions of high current density were studied in detail.[31, 32, 163–178] The conditions for formation of ferrate(VI) were found,[31, 32, 168–173] qualitative notions of the mechanism of this process were developed and explanations were offered for the decomposition of concentrated ferrate(VI) solutions to form iron(III) hydroxide. Abnormal properties of ferrate solutions were observed. The detailed studies of these properties allowed conclusions to be made about the existence of ferrates(IV) in alkaline media (previously, it was believed that these compounds are unstable in aqueous solutions) as well as about the occurrence of FeO_4.[31, 32] These compounds were identified by electronic spectroscopy of solutions, Mössbauer spectroscopy and some other methods. The justified assumptions were made that ferrate(VI) may undergo disproportionation and thermal stimulation of the latter afforded Fe^{VIII} and Fe^{IV} derivatives.

Iron tetroxide is very unstable. It can be isolated in a relatively pure form by extraction from solutions of ferrates in CCl_4. The extracts were distilled at 30 °C to give products in yields no higher than 25%–30%. These properties were used in the preparation of highly pure iron.[179–181] Solutions of Fe^{VIII} undergo autocatalytic decomposition to Fe^{III} hydroxide and can exist only when the concentration of iron is lower than 0.01 mol litre^{-1}. The Mössbauer spectra (77 K) of aqueous–alkaline systems containing Fe^{VIII} have a singlet line belonging (judging from the value of the chemical shift δ) to the highest valent form of iron.[32]

Ferrate(VI) in an aqueous–alkaline medium is so stable that its solutions under normal conditions can be stored for at least two years. This compound is formed not only in the course of the above-mentioned disproportionation but also under prolonged action of oxygen on alkaline solutions of Fe^{III} hydroxo complexes.[178–181]

The data on FeO_4 essentially supplement the known regularities of the Periodic system and, in addition, make it possible to establish a qualitative correlation between the stability of the compounds and the occupancies of the orbitals determined by quantum-chemical methods.

2. Copper, silver and gold

The data on OS of copper, silver and gold are given in Table 4. For this group of elements, OS $\geqslant +3$ are unstable, although, strictly speaking, even OS of +2 is unstable. For example, one of the manifestations of the effect of variable valence, *viz*., the fluctuation of the charge state, is observed for Cu^{II} ions. Apparently, this results in such a value of the redox potential $E^{\circ}_{Cu^{II}/Cu}$ that the Cu^{II} ion can be considered as an oxidant.

Table 4. Oxidation states of copper, silver and gold.

OS	Cu	Ag	Au
+1	+ (see [a])	+ (see [a])	+ (see [a])
+2	+ (see [a, b])	+ (see [b, d])	? (see [b])
+3	+ (see [c, d])	+ (see [c, d])	+ (see [a])
+4	+ (see [c, d])	? (see [b])	? (see [b])
+5		+ (see [d])	+ (see [d])

[a] Known in many compounds. [b] Undergoes disproportionation. [c] For oxides. [d] For fluorides.

The problem of the existence of the highest valent forms for Cu, Ag and Au is still not completely solved. This is particularly true for gold. The first Au^V compound, *viz*., the fluoro complex with the bulky $Xe_2F_{11}^+$ cation, was prepared only in 1972.[182] Since that time, some other Au^V compounds have been synthesised. In particular, AuF_5 and fluoro complexes with cations of alkali and alkaline-earth metals were prepared. However, no compounds with ligands other than fluoride were found.[183] The questions of whether Au^{IV} can be isolated and whether OS higher than +5 can be realised are still open. The same is true for silver compounds. Thus, only the Ag^V derivative with composition $Cs_2Ag^V_{1/2}Ag^{III}_{1/2}F_6$ is known.[184]

These problems have been considered many times.[150, 151, 185–197] New binary (AgF_3) and complex fluorides of Cu^{III}, Ag^I, Ag^{II}, Ag^{III}, Au^{III}, Au^V and $Ag^{III,V}$ with various outer-sphere cations were synthesised and studied. Many of the synthetic reactions of these compounds have been examined and the factors that affect the yields of the products and, consequently, the stabilisation of the corresponding OS have been revealed.[197] Finally, data which can be interpreted in the context of disproportionation of Au^V were obtained in studies of thermolysis products of Au^V fluoro complexes.[150] In fact, there is no direct evidence for the presence of a disproportionation product, *viz*., of a fluoride more enriched with fluorine than AuF_5, in the gaseous phase.

The data on the preparation of Cu^{IV} as Cs_2CuF_6 and Cu^{IV} oxide were reported in Refs 198 and 199, respectively. The latter experiments were carried out under high oxygen pressure. The oxide contains Cu^{III} and Cu^{IV} stabilised in the perovskite lattice with composition $La_{1-x}Sr_xCuO_3$ ($0 \leqslant x \leqslant 0.25$).

The formation of mixed-valence states is typical of Cu, Ag and Au both in the fluoride and oxide systems. In oxide superconductors and related compounds, these states of copper are of great importance. In superconductors, the OS of copper varies from +1 to +2.33. In this case, the π-orbitals of oxygen atoms make significant contributions to the corresponding molecular orbitals. The mixed-valence states[200, 201] are responsible, for example,[202] for a 'charge-stabilised' distortion of $NaBa_2Cu_3O_6$. Of the recent works in this field, let us note Refs 203–205. The unusual properties of gold oxides in oxide films were described.[206, 207] In this connection, recall the effects associated with the dynamics of the electron density in the solid phase.[71] The unit cell can contain metal ions in different OS that occupy crystallographically non-equivalent positions, metal ions in different OS that occupy equivalent positions and, finally, metal ions in the so-called fluctuating state where fast oscillations (which are equivalent to electron transitions between different OS) of electron density occur at each lattice centre. The existence of the mixed-valence state is an indication of valence instability. This problem as well as the factors favourable for disproportionation were considered.[48] The existence of copper in the mixed-valence state ($Cu^{III,IV}$) in oxides is indicative of a decrease in the stability of OS +4 of copper compared to that observed in the fluoride due, apparently,

to the presence of the essential π-component of the metal–ligand bond in the oxide. Taking into account the existence of copper in the Cu^{III}/Cu^{IV} state, it is believed that +4 is the extreme oxidation state for copper.

3. Heavy platinum elements

Difficulties emerge in the realisation of the highest OS for heavy 5*d* transitions elements (Table 5). This is particularly true for Ir, Pt, Au and Hg. It can be seen that the maximum oxidation state attained for platinum metals is equal to +6, which is, apparently, far from the extreme value. The main and most reliable information on the properties of the strongly oxidised ions of the above-mentioned elements concern predominantly their fluorides, although scattered data on oxide systems have been recently reported.

Thus attempts were made to synthesise iridium compounds in the highest OS under high oxygen pressure (it is known [211,212] that high pressure favours attainment of unusual OS of transition elements).[208–210] The properties of a new series of oxides with the distorted K_2NiF_4 structure of composition $A_2MIr^{VI}O_6$ (A = Ba or Sr; M = Sr, Ca, Mg or Zn) containing iridium in OS of +6 were reported.[208,209] The structural and magnetic properties of the $Sr_2Rh^{IV}O_4$ and $Sr_2Ir^{IV}O_4$ compounds, which are analogues of La_2CuO_4, were studied.[213] X-Ray and neutron diffraction studies demonstrated the distortion of the ideal structure of the K_2NiF_4 type. Oxoplatinates with composition $Ln_2MPt^{IV}O_6$ (Ln = La, Pr, Nd, Sm, Eu or Gd; M = Mg, Co, Ni or Zn) were prepared.[214]

Note also the electrochemical studies of hydroxo complexes of iridium in OS of +4, +5 and +6 [83,84] and studies aimed at preparing platinum and iridium compounds in the highest OS in alkaline solutions.[215–219] Solutions of hydroxo complexes of platinum and iridium were treated with ozone and the resulting compounds were studied by various methods, including ESR, electronic absorption spectroscopy, cyclic voltammetry and chemical analysis. It was established that the platinum hydroxo complexes afforded the previously unknown platinum superoxo complexes $[Pt(OH)_5(O_2^-)]^{2-}$, $[(OH)_5Pt(\mu\text{-}O_2^-)Pt(OH)_5]^{3-}$ and $[(OH)_4Pt(\mu\text{-}O_2^-)(\mu\text{-}OH)Pt(OH)_4]^{2-}$. In the case of iridium, hydroxo complexes of iridium in OS of up to +6 inclusive were detected in solution along with the peroxo and superoxo complexes of iridium of the $[(OH)_5Ir^{IV}(\mu\text{-}O_2^-)Ir^{III}(OH)_5]^{5-}$ {or $[(OH)_5Ir^{III}(\mu\text{-}O_2^-)Ir^{III}(OH)_5]^{5-}$} type.[218] This suggests that OS of +6 for iridium can be attained even under rather mild conditions (in solution), which indicates that treatment of solutions of hydroxo complexes with oxidants under more drastic conditions has considerable promise.

V. Matrix oxidation state stabilisation

Recently, the so-called method of matrix OS stabilisation has been developed. This method is based on the fact that the tracer atoms incorporated into the crystalline matrix are interchangable with the metal atoms of the base upon heating. Thermal treatment is apparently one of a few procedures used in this case because the mechanism of transfer of the atoms is obviously of a diffusion character and the diffusion is enhanced at higher temperatures. The efficiency of the exchange reaction is associated with the possibility of the change in the size of tracer atoms or of a change in the electronic configuration (and, consequently, in OS) of the above-mentioned atoms, *i.e.*, with the lability of the corresponding electron cloud. The crystal field of the matrix 'forces' the doping ions to behave as the electron cloud in the crystal lattice, which is in some cases accompanied by charge transfer from one metal atom to another,[220] *i.e.*, by a change in OS.

The geometrical criteria (ionic radii, local symmetry, *etc.*) are of great importance because they reflect the effect of the thermodynamics of the mixed matrix–tracer system. The stability of OS should be determined to a large extent by the isomorphism rules because the geometry of the vacancy into which a transition metal ion is inserted plays a great role in the stabilisation of the latter.

The effect of the matrix on the properties of the doping ions can be illustrated by a change in the colour of Cr^{III} ions placed at the matrix nodes with different local symmetry. In corundum (α-Al_2O_3), beryl ($Al_2Be_3Si_6O_{18}$) and kyanite (aluminosilicate, Al_2SiO_5), the Cr^{III} ions are red, green and blue, respectively.[221] Shifts of the absorption bands in energy depend on various factors, including the coordination number, and the absorption bands corresponding to the charge transfer depend on the valence transitions or on the stability of OS. For example, a change in OS of cerium in the same matrix, *viz.*, in ZrO_2 (fianites), leads to a change in the colour from bright red-claret (Ce^{IV}) to yellow-orange (Ce^{III}).[222]

Many researchers use the matrix stabilisation of the highest OS in spite of the fact that the lattice contributions to the total energy are insignificant. This method was used for preparing laser crystals doped with transition metal ions (see, for example, Refs 223 and 224). However, note that it is difficult to obtain metal ions in high OS in these subjects because of their specificity.

Table 5. Known oxidation states of heavy transition elements.

OS	W	Re	Os	Ir	Pt	Au	Hg
+1		+ (see [a])	+ (see [a])	+ (see [a])		+ (see [c])	+ (see [c])
+2	+ (see [b])	+ (see [b])	+ (see [d])	+ (see [a])	+ (see [c])	+ (see [f,g])	+ (see [c])
+3	+ (see [d])	+ (see [a,b])	+ (see [d])	+ (see [c])	+ (see [g])	+ (see [c,d])	+ (see [j])
+4	+ (see [b,e])	+ (see [c])	+ (see [c])	+ (see [c])	+ (see [c])		
+5	+ (see [c])	+ (see [c])	+ (see [d])	+ (see [e,f])	+ (see [f])	+ (see [f,g])	
+6	E (see [d])	+ (see [d])	+ (see [e,f])	+ (see [e,f])	+ (see [i])	? (see [i])	
+7		E (see [d])	+ (see [d])			? (see [i,j])	
+8			E (see [e,h])				− (see [j])
+9				? (see [k])			
+10					− (see [j])		

Note. The following notations are used: E, the highest OS, which is, apparently, the extreme one; 'minus sign,' this OS is absent.

[a] Known, for example, in carbonyls and complex phosphines. [b] Known, for example, in halides and cyanides. [c] Known in many compounds. [d] Known in oxides and halides. [e] For oxides. [f] For fluorides. [g] Disproportionation occurs. [h] For hydroxo complexes. [i] A very unstable higher fluoride with an unknown composition formed upon heating of fluoro Au^V complexes. [j] See the discussion in the text. [k] The formation of this OS in a compound formed upon β-decay of $^{191}OsO_4$ was reported.

In matrices which are more suitable for stabilisation (for example, in $BaM^{IV}O_3$, where M = Ce, Th or Zr), Pr^{IV}, Tb^{IV}, Nd^{IV} and Dy^{IV} were obtained.[128–130] Interestingly, it is possible to obtain Nd^{IV} in all the above-mentioned matrices, while Dy^{IV} was obtained only in $BaCe^{IV}O_3$. The Mn^{III},[224] Cr^{IV} and Cr^{V} as well as Fe^{VI} ions[225,226] are stabilised in matrices of garnets, chromates and sulfates (the systems were prepared from solution) and Tb^{IV} ions are stabilised in ($SrMgF_4:Tb^{IV}$)-phosphors (prepared in the solid phase).[227]

In studies of matrix oxide systems involving oxoferrates and oxoruthenates,[33,34,228–236] the conditions for doping these matrices with Fe^{n+} and Co^{n+} ions (OS were established by Mössbauer spectroscopy with the use of ^{57}Fe and ^{57}Co isotopes) were found. Of the most interesting results, note the stabilisation of Co^{VI} ions in the ferrate $Cs_2Fe^{VI}O_4$ (see Refs 33 and 34) and the stabilisation of Fe^{VI} ions in the mixed-valence compound with composition $Cs_3(Ru^{VI}_{1/2}Ru^{VII}_{1/2}O_4)$.[232,235]

Attempts to attain the Fe^{VII} state are of particular interest. This OS can be realised for Fe. Thus it was concluded[165] that the disproportionation of FeO_4^{2-} ions (in alkaline media) occurs according to the following scheme:

$$2Fe^{VI} \rightleftharpoons Fe^{VIII} + Fe^{IV}.$$

Since a two-equivalent exchange occurs, the intermediate one-electron conversion with the participation of Fe^{VII} could be expected in accordance with Scheffer's principle. It was attempted to solve the problem of stabilisation of this OS by placing ^{57}Fe in the $Cs_3(Ru^{VI}_{1/2}Ru^{VII}_{1/2}O_4)$ matrix. In this ruthenate, the iron ion is stabilised primarily in the Fe^{VI} form. However, an unstable satellite was also observed in the slope of the intense line in the Mössbauer spectrum. The chemical shift value of this satellite corresponds to that expected for Fe^{VII}.[232,236] Unfortunately, there is no more convincing evidence for the presence of Fe^{VII} in this system. According to the data of Mössbauer spectroscopy (4 K),[229,237–241] the Fe^{VII} state can also be stabilised in the Na–Fe–O system at a molar ratio [Na]:[Fe] > 50:1 (at lower ratios, only Fe^{IV} compounds are formed[242]).

Unlike other researchers, the authors of the publications[229,237–242] applied oxidation processes using sodium and cesium peroxides under rather mild conditions. The latter are suitable for the realisation of high OS if the strongest oxidants (Na_2O_2 and CsO_2) as well as an efficient stabilising agent (in particular, Cs^+ cations) are present in the reaction mixture.[43] In addition, peroxides as such can stabilise the highest OS of, for example, iron and cobalt on condition that their contents in the reaction mixtures are low.[229,241] Highly reactive reagents (precursors) which are formed, for example, upon ultrasonic treatment show promise. It is by this procedure that specimens of highly disperse Fe_2O_3 were prepared.[243] The procedures for the preparation of the corresponding precursors have been summarised.[244]

VI. Valence possibilities of transition elements

It was hypothesised that the heaviest 5*d* elements can attain high OS,[48] which can be realised for Ir, Pt, Au and Hg in the tetrahedral oxo ions $MO_4^{n\pm}$. Estimates of the energies of molecular orbitals which were obtained by the scattered wave X_α method for a series of tetraoxo anions $M^{VII}O_4^-$ of the third-row elements[245,246] indicate that rather stable compounds can be formed. Quantum-chemical and thermodynamic calculations were performed for the tetrahedral MO_4^q ions isoelectronic with OsO_4 (M = Ir, Pt, Au or Hg, $q = +1, +2, +3$ or $+4$, respectively).[49] Quantum-chemical calculations were carried out with the use of quasirelativistic and relativistic pseudopotentials (*cf.* Ref. 247), which are believed to be very reliable.

Ab initio calculations for the $Ir^{IX}O_4^+$, $Ir^{VII}O_4^-$, $Pt^{VIII}O_4^0$ and $Au^{VII}O_4^-$ ions demonstrated[49] that the potential surfaces have minima. For the $Pt^{X}O_4^{2+}$ and $Au^{IX}O_4^+$ cations, minima are also observed but they are apparently too shallow to expect the formation of more or less stable compounds. An analogous conclusion can be drawn on the basis of the results of thermodynamic calculations. The main outcome of the study[49] was the conclusion that transition elements in very high OS (which have not yet been realised), up to +10 inclusive, can theoretically occur.

It was demonstrated[49] that the probability of the existence of $Hg^{VIII}O_4^0$ is distinct from zero because calculations gave a reasonable value for the internuclear Hg–O distance of 2.12 Å (HgO_4^{2+} ions and all the more so, HgO_4^{4+} ions are unstable). Probably, mercury compounds in OS of lower than +8 are rather more stable.

For mercury and its analogues (Zn and Cd), +2 is still considered to be the highest OS. Note that the short-lived complex of trivalent mercury with composition $[Hg(cyclam)](BF_4)_2$ was reported,[248] although these data require additional proof. It was suggested that an unstable intermediate containing Hg^{III} is formed upon fluorination of organomercurials with xenon difluoride.[249,250] Based on the results of X-ray photoelectron spectroscopy of mercury copper–oxide superconductors with composition $HgBa_2(Ca_{0.86}Sr_{0.14})_2Cu_3O_{8+\delta}$, it was concluded that these superconductors contain Hg^{III}.[251,252] On the basis of the general regularities of the Periodic system, Jorgensen also believed that the possibility exists of attaining high OS for mercury.[37] He reasoned that the existence of $I(5d)$ of ~ 14 eV for mercury(II) fluoride may favour oxidation of Hg^{II} to Hg^{III} or Hg^{IV}, particularly taking into account that HgF_2 crystallises in the fluorite structure with a low lattice energy. The realisation of the $5d^8$ configuration and consequently of Hg^{IV} in the square-planar HgF_4 molecule is more probable than the $5d^9$ configuration and Hg^{III}.

In this connection, the publication[38] in which the molecular and electronic structure and the stability of HgF_4, ZnF_4 and CdF_4 were compared is of fundamental importance. The possibility of stabilisation of HgF_4 upon anionic complexation was considered. Calculations were performed with the use of the same pseudopotentials as those used previously[247] for HgF_2. It was shown that the fluoride HgF_4 may well exist in the gaseous state.[38] To the contrary, the existence of CdF_4 and all the more ZnF_4 is highly improbable. In addition, it follows that complexation does not enhance stabilisation of Hg^{IV} with respect to Hg^{II} in anions.[38] The conclusion that complexation affects only slightly the stability of Hg^{IV} is unexpected because this is considered as one of the ways of stabilising the highest OS of *f* and *d* transition elements.[39,40] Since Hg^{IV} should exhibit the properties of *d* transition elements, the statement that the formation of the HgF^{x-}_{4+x} anionic complexes has a favourable effect on the stability of Hg^{IV} should be fulfilled. The introduction of an equivalent amount of cations into the system containing anions decreases substantially the total energy of the system. In this case, the mutual cation–anion influence should occur and stabilisation should be realised through the electrostatic forces. In particular, this is consistent with the results of calculations of the electronic structures of the $M^{V}F_6^-$ ions (M = Hf, Ta, W, Re, Os, Ir, Pt, Au or Hg)[253] by the spin-polarisation discrete variation X_α method. The change in electron affinity in the $HfF_6^- \rightarrow HgF_6^-$ series as well as the experimental data on the stability of the complex fluorides of Os^{V}, Ir^{V}, Pt^{V} and Au^{V} (compared to the data on the corresponding MF_5) indicate that the effect of complexation does exist. Thus the temperature of decomposition of complex fluoroaurates(V) is 100 °C higher than that of AuF_5.[45,150,192] Hence, the conclusion that coordination has no effect on the stability of higher mercury fluorides is questionable although it was not disproved (HgF_4 or other Hg^{IV} fluorides have not been obtained yet despite attempts, as can be judged from the published data,[38] aimed at their synthesis).

We emphasise that in the above-mentioned theoretical studies, only the presence of the minimum on the potential surface was noted, while the depth of this minimum can be determined only

experimentally. Thus derivatives of $Cs^{III}-Cs^{IX}$ and krypton oxides‡ have not yet been obtained, although calculations predicted that they can exist.[255] Apparently, this is also true for HgF_4.

VII. Regularities of changes in the extreme oxidation states of transition elements

The highest OS of transition elements (according to the experimental data and results of quantum-chemical calculation)[89] are shown in Scheme 1. The extreme OS (E) are separated from the higher OS by a thick line, which assumes that the latter cannot be attained. It can be seen that the values of the extreme OS in the series of transition metals increase, reach a maximum and then decrease. This character of the change in the maximum OS is one of the main regularities of the Periodic system. For some OS, the experimental data are lacking but there is reason to hope that such information will be obtained. In relation to the aforesaid, it is necessary to make some comments.

For the first-row transition metals, the maximum OS is observed for iron (+8). The existence of Mn^{VIII} in tetraoxide MnO_4^0, which is formed upon photodissociation of the MnO_4^- ion, is suggested on the basis of spectroscopic data.[256] Probably, this conclusion is erroneous. For cobalt, +6 is the highest OS.[33,34] This state was identified by emission Mössbauer spectroscopy. The detection of OS by this method may indicate that it is highly unstable. In view of this fact, it is believed that +6 is the extreme OS for cobalt. For Ni, +4 is the highest OS attained. It is assumed that Ni^{VI} can be realised (handbooks even contain the E° value for the Ni^{VI}/Ni^{II} pair). In our opinion, the existence of Ni^{VI} is still an open question. The preparation of Ni^{V} is more probable. Moreover, the identification of the OS in this case is a very complicated problem. The stability of Ni^{VI} and Ni^{V} derivatives should be rather low and probably the only suitable technique for observing OS is Mössbauer spectroscopy which can detect the chain of transformations $^{57}Ni \rightarrow {}^{57}Co \rightarrow {}^{57}Fe$.

The detection of particular OS in studies by emission Mössbauer spectroscopy [provided that radiative transitions (known as post-effects) are absent] is very revealing. In fact, for the $A \rightarrow B$ process where compound B has OS which can be observed by Mössbauer spectroscopy, $a_A \sim 1$ and $a_B = 10^{-8}$ (a is the activity). The latter value can readily be obtained on the assumption that the activity of the source was ~ 1 mCi (^{57}Co). Then $k_{eq} = a_B/a_A \sim 10^{-8}$ and $\Delta_r G^\circ = RT\ln k_{eq}$ is about 50 kJ mol^{-1}, *i.e.*, it is impossible to obtain macroscopic amounts of a compound containing the desired OS.

For the second-row transition metals (see Scheme 1), the maximum OS is attained for Ru(+8). Compounds containing Rh^{VI} and Pd^{V} were described. On the basis of the published data,[246] both states can hardly be assigned to the limiting states. In this connection, the question of whether higher OS are possible remains open. In the third-row transition elements, the maximum OS for iridium is +9[48,49] (apparently, this is the extreme OS), while OS +10 can be attained for platinum.[49] The probability of occurrence of the nona- and decavalent states for the elements is an open question.

According to Abegg's rule, each element may have a set of OS consisting of no more than 8 values. It is known[37] that this rule is fulfilled for the main-group elements and for the post-transition elements. Only four exceptions to this rule are known, namely, Mn, Ru, Re and Os, for which ten OS can be realised.[37] Assuming that OS of +10 and +9 can be attained for platinum and iridium, respectively, and thus postulating sets of 10 OS for these elements, we extend the series of the above 'exceptions.' Without considering the nature of this phenomenon (which is, of course, governed not only by the electrostatics of metal–ligand interactions), we emphasise that the above 'exception' for transition elements is apparently the rule. Evidently, the presence of a particular set of OS for the element as well as the maximum valence are determined primarily by the principle of the arrangement of the Periodic system (the so-called 'Aufbau' principle; this follows from the ideology of the publication[37]) which is based on thermodynamic factors, primarily on the energies of the detachment of electrons from the free atom. This can be judged, for example, from the values of the ionisation potentials[257,258] of atoms§ realising that it is the differences between the ionisation potentials, which can characterise the tendency for OS stabilisation, rather than the absolute values of these potentials that are of importance. Analysis of the ionisation potentials demonstrated that it is necessary to overcome an energy barrier the value of which is

Scheme 1

Metal	Oxidation state of the metal								
	2+	3+	4+	5+	6+	7+	8+	9+	10+
Sc		E							
Ti			E						
V				E					
Cr					E				
Mn						E			
Fe							E		
Co					E				
Ni			H	??					
Cu			E						
Zn	E								
Y		E							
Zr			E						
Nb				E					
Mo					E				
Tc						E			
Ru							E		
Rh					H	??			
Pd				H					
Ag				E					
Cd	E								
La		E							
Hf			E						
Ta				E					
W					E				
Re						E			
Os							E		
Ir					H	??	??	?(see [a])	
Pt					H		??	??	see [b]
Au				H			see [b]	see [b]	
Hg	H	see [c]	see [b]				see [b]		

The following notations are used: H, the high OS is known, but it is unclear whether it is the extreme value; ??, the data are lacking, but there is the probability that this state can be attained.

[a] The data were not confirmed. [b] According to the results of quantum-chemical calculations, this OS can be attained.[49] [c] The possibility of formation of derivatives upon fluorination of organomercurials at low temperature was reported.[249,250]

‡ It was reported that a krypton compound with the orthotellurate ligand was presumably obtained though under cryogenic conditions.[254] This compound exploded even under these conditions. More detailed data in support of the individuality of this compound and of the presence of the Kr–O bond are lacking.

§ An analogous procedure was used in the analysis of the regularities of the changes in the ionisation potentials of atoms of the heavy transition elements.[48] Speculative conclusions obtained on this basis were subsequently confirmed by direct quantum-chemical calculations.[49]

reflected in the stability of the OS, on going from one OS to another.

These barriers can be overcome in chemical (or in physical) processes. The latter is illustrated in the observation of a high OS for the metal atoms upon β-decay of ^{191}Os,[259] Am and Bk in oxides,[15,16] which provides short-lived $Ir^{IX}O_4^+$, $Cm^{VI}O_2^{2+}$ and $Cf^{V}O_2^+$ ions, respectively. In other words, the existence of OS +9 or +10 for some elements does not contradict the principles of construction of the Periodic system.

It was of interest to verify the regularities of the changes in the extreme OS and the observations of OS higher than the extreme values. On the one hand, the fundamental regularity as declared above seemingly does not allow for the formation of these OS. On the other hand, these OS are not theoretically forbidden and only energy barriers occur, which can be overcome in some cases, as demonstrated above.¶ Presently, there is no point in going through all the details because the experimental data are lacking. However, attempts can, in principle, be undertaken to obtain this information, for example, in experiments on bombardment of solid and liquid targets with heavy highly charged ions. For example, calcium targets were bombarded with Ar^{12+} ions,[262,263] helium was treated with C^{6+}, N^{7+}, O^{8+}, Ar^{16+}, I^{16+} and Xe^{30+} ions[264] and the recombination of Kr^{34+} ions on hydrogen molecules was considered.[265] Evidently, the appearance of an almost bare nucleus in the matrix should cause a cascade of Auger electrons. These secondary processes are known and are being studied. For example, the manifestations of the secondary processes in the K_α spectra which were observed in experiments on bombardment of sulfur targets with Ar^{5+} and Xe^{8+} ions were analysed.[266] Actually, the problem of OS stabilisation was not solved in the papers cited because ions and targets evidently were not optimum (in this context, the above-discussed studies on the matrix OS stabilisation are of importance). The questions are how long these superhigh OS live and whether these states can be detected by the available physical methods.

To summarise, the present review considers the state-of-the-art of the problem of the existence and stabilisation of the highest and extreme valent forms of transition elements. In the discussion of these problems, many authors (see, for example, Refs 23 and 29) attempted to reveal the relationship between the electronic structures of the atoms and the properties of the compounds. Evidently, this relationship can be also revealed in the present review. However, *d* transition elements (particularly, heavy elements) are characterised by a high degree of covalence, which makes these correlations poorly informative. Hence, we restrict ourselves to the discussion of the chemical evidence and the statement of empirical regularities. The advantage of the empirical method is its independence from the electronic structure and the inherent nature of the subjects under consideration. This is of particular importance when the data are scarce as in the case of elements in the highest unstable OS which are few in number. At the same time, the discussion of the general situation on the basis of the available reliable quantum-chemical and experimental data allows us to offer the hypothesis that superhigh and short-lived OS exist and to suggest the procedure for its verification.

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¶ This question for main-group elements was considered by Sidorov,[260] who has suggested that BeF_3 and AlF_4 can be obtained. However, more recent studies demonstrated[261] that attempts to obtain the above compounds and, consequently, OS higher than the extreme values (+2 for Be and +3 for Al) in chemical processes failed.

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