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Periodicity of the change in properties in the series of *d*- and *f*-elements

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ABSTRACT. Many physicochemical properties in series of *d*- and *f*-elements change periodically with change in the number of *d*- or *f*-electrons in the d^q- or f^q-electron configurations. In the lanthanide and actinide series for a fixed electron configuration, the f^q-periodicity of the change in properties is called the tetrad or double–double relationship.

A number of properties of *d*-elements, lanthanides, and actinides depend on the initial d^q-, f^q- and final d^{q-1}-, f^{q-1}-electron configurations. These properties include the ionisation potentials of the free atoms and ions, electron affinity, redox potentials, excitation energies, and enthalpies of the decomposition and disproportionation of the halides, oxides, chalcogenides, and pnictides of the lanthanides and actinides, the oxidation state in compounds with variable oxidation states, etc. The present review analyses the regularity of the change in these properties in the lanthanide and actinide series, demonstrates the nature of the change in these properties, formulates a simple rule making it possible to predict unknown properties, and carried out an extensive comparison with the properties of *d*- and *p*-elements and their compounds. The properties of the trans-actinide *g*- and *h*-elements are predicted.

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I. Introduction

With increase in the atomic number in the series of *f*-elements, the *f*-levels are gradually filled, leading to a similarity between the lanthanides and actinides. The similarity in many properties of their trivalent states is a long established fact. At the same time, the lanthanides and actinides exist in higher oxidation states: $Ln^{III,IV}$ and $An^{III-VII}$. In this way they show a similarity to the *d*-elements. Thus the actinides, showing a qualitatively new increase in the complexity of the electronic structure, resemble the lanthanides, but in their high and highest oxidation states they show a definite analogy with the *d*-elements. There is thus an overall regularity in the properties of the actinides, lanthanides, *d*-elements, and their compounds.

A number of recent papers have compared all these elements. Everyone who has studied, on the one hand, solid state physics, and on the other hand the chemistry of the simple and coordination compounds inevitably draws attention to the differences in the focus of the theoretical approaches in these branches of science. Qualitatively, however, both approaches lead to the conclusion that the light actinides are the analogues of the 3*d*-elements, rather than the 4*f*-elements. In each series, the behaviour of the electrons changes from delocalised bonding behaviour to localised non-bonding behaviour. At the same time, a group of elements show intermediate behaviour of the electrons: Ce, Pr, U, Np, Pu, Mn, and Fe. Subsequent analysis of experimental and theoretical data[1–3] has shown that there is a definite periodicity in the change in the physicochemical properties with change in the atomic number of the element in the *d*- and *f*-series. This periodicity covers a wide range of properties of both the free atoms and ions and their compounds, is general in character, and extends to the super-heavy compounds in the *g*- and *h*-series which have not yet been obtained.

II. Systematics of the properties of the free atoms and ions

Many physicochemical properties P of the lanthanides Ln and actinides An change periodically with change in the atomic number of the element or in the number of electrons q in a fixed f^q-electron configuration in accordance with the periodic change in the orbital quantum numbers L_q of the normal terms. Many examples of the existence of this periodicity can be given:[4] the change in the standard energy of extraction of the trivalent lanthanides, the ionic radii of the *d*- and *f*-elements in different charged states, the critical temperature of the appearance of superconductivity of the metals of the *d*-series, etc. In the final analysis, the periodic change in these properties is determined by the characteristic dependence of the quantum numbers L_q on q (Fig. 1) in the corresponding l^q-electron configurations (l = *d*-, *f*-, *g*-, and *h*-elements). Fig. 1 shows that in each series there is a characteristic double–double effect in the change in the properties P: d^0-d^5-d^{10}, f^0-f^7-f^{14}, g^0-g^9-g^{18}, h^0-h^{11}-h^{22}. Moreover, as a consequence of the two-fold symmetry with respect to the central pair in each half of the series d^2-d^3, d^7-d^8, f^3-f^4, f^{10}-f^{11}, g^5-g^6, g^{14}-g^{15}, h^7-h^8, h^{18}-h^{19} for the quantum numbers L there are respectively pairs of triads, tetrads, pentads, and hexads in the *d*-, *f*-, *g*-, and *h*-series.

Thus in the series of *s*-, *p*-, *d*-, *f*-, *g*-, and *h*-elements it is possible to construct definite sequences of electron configurations depending on the number of electrons and the quantum numbers L_q: s^0-s^1, s^1-s^2; p^0-p^1, p^2-p^3; d^0-d^2, d^3-d^5; f^0-f^3, f^3-f^7; g^0-g^4, g^5-g^9; h^0-h^5,

h^6-h^{11}. Similar sequences can be constructed in the second halves of the series, with a displacement by a number of electrons equal to the number of electrons in the half-filled levels.

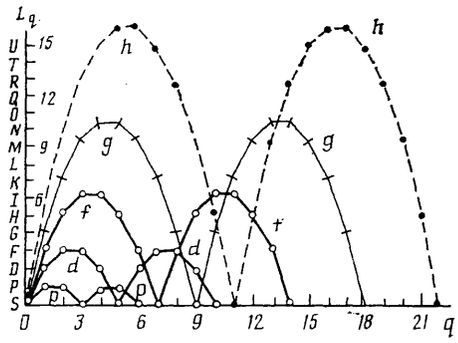


Figure 1. Plot of the quantum numbers L_q against the number of electrons q in the series of *s*-, *p*-, *d*-, *f*-, *g*-, and *h*-elements.[12]

1. Redox processes

If the electron configurations of the atoms or ions change in a reaction, the periodicity of the change in properties depends on the quantum numbers L_q and L_{q-1} in the initial and final electron configurations f^q and f^{q-1} or d^q and d^{q-1}. The ionisation equilibrium $f^q \rightleftharpoons f^{q-1} + e$ and $d^q \rightleftharpoons d^{q-1} + e$ ($L_q \rightleftharpoons L_{q-1}$), corresponding to a redox reaction, can be examined. It will be assumed that there exists a temperature range in which there are only two kinds of ion containing q and $q-1$ electrons; for example doubly- and triply-ionised, or triply- and quadruply-ionised ions, etc. The condition for chemical equilibrium can then be written as

$$E_0/kT = \ln(\zeta_q n_q / \zeta_{q-1} n_{q-1}), \quad (1)$$

where E_0 is the absolute magnitude of the difference in the energies of the non-split normal terms of the l^q- and l^{q-1}-electron configurations, n_q and n_{q-1} the numbers of ions in these configurations, and ξ_q and ξ_{q-1} the values of the corresponding distribution functions or the multiplicities of the degeneracy of the normal terms with respect to the quantum numbers M_L for fixed spin quantum numbers S. The parameter α giving the probability that an ion has the oxidised electron configuration d^{q-1} or f^{q-1} can be introduced. In the high-temperature limit $kT \gg E_0$,

$$\alpha = \frac{n_{q-1}}{n_q + n_{q-1}} = \left[\left(1 + \frac{\zeta_q}{\zeta_{q-1}}\right)\exp(-E_0/kT)\right]^{-1} = \frac{2L_{q-1}+1}{2L_q + 2L_{q-1} + 2}, \quad (2)$$

which corresponds to ionisation equilibrium. The dependence of α on q for *p*-, *d*-, *f*-, *g*-, and *h*-elements is shown in Fig. 2*a*, which demonstrates the periodicity in the change in the redox properties in each half of the series with increase in the atomic number or the number of electrons q. This periodicity is revealed in the sharp–retarded–sharp change in properties in each half of the series. The sharpest change in properties is observed on going from the first to the second half of the series. For the elements of the *f*-series, with allowance for the equalities

$$L_q = q(7-q)/2, \; q \leqslant 7; \; L_q = (14-q)(q-7)/2, \; q > 7 \quad (3)$$

it is possible to rewrite Eqn. (2) as follows

$$\alpha = \frac{9q - q^2 - 7}{16q - 2q^2 - 6}, \; q \leqslant 7; \; \alpha = \frac{23q - q^2 - 119}{44q - 2q^2 - 216}, \; q > 7. \quad (4)$$

This dependence of α on q covers a wide range of properties: ionisation potentials, electron affinity, redox potentials, excitation energies, etc. The section of the plateau corresponding to the retarded change in properties is not observed for the *p*-elements; for two-electron reactions $d^q - d^{q-2} + 2e$ the section of the plateau becomes indistinct, and the dependence of α on q is close to linear.

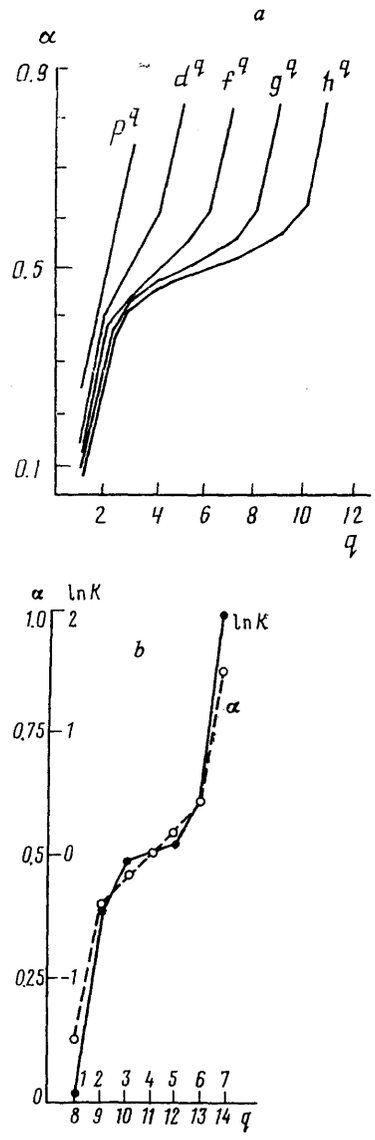


Figure 2. Dependence of the parameter α on the number of electrons for various elements[4] (*a*) and the dependence of the parameters α and $\ln K$ on the number of electrons (*b*) in the series of *f*-elements.

Similar conclusions are reached for the constants K of the ionisation equilibrium $f^q \overset{K}{\rightleftharpoons} f^{q-1} + e$ for a monatomic gas consisting of f-ions. The free energy for this reaction, $F = -RT \ln K$, depends on the number of electrons q and $q-1$, the quantum numbers L_q and L_{q-1}, and the ionisation energy I_q (Fig. 2*b*). At $T \simeq I_q$ the periodicity of $\ln K$ with change in q is determined by the difference $\Delta L = L_{q-1} - L_q$

$$\ln K \approx 2\,(L_{q-1} - L_q)\,(L_{q-1} + L_q + 1)^{-1}. \qquad (5)$$

The section of the plateau corresponding to elements for whose oxidised and reduced forms the values of ΔL are low, are shown in Fig. 2*b*.

2. The rule of intervals in redox processes

In the *LS*-coupling approximation, the *d*-, *f*-, *g*-, and *h*-levels have internal symmetry, according to which, for the normal terms of the ions with the electron configurations l^q, where $l \equiv d, f, g, h$, the quantum numbers L_q and S_q are given by the equations

$$\text{for } q<7\text{: } L_q = q(2l+1-q)/2,\ S_q = q/2;$$
$$\text{for } q>7\text{: } L_q = (4l+2-q)(q-2l-1)/2,\ S_q = (4l+2-q)/2. \qquad (6)$$

Eqns. (2) and (6) lead to the simple rule of intervals in the change in the properties P_q with change in q in the *d*- and *f*-series of elements.

For the *f*-elements:

$$\text{for } q \leqslant 7,\ c=0\text{: } (P_{1+c}+P_{7+c}):P_{4+c} = (P_{2+c}+P_{6+c}):P_{4+c} = (P_{3+c}+P_{5+c}):P_{4+c} = 2;$$
$$\text{for } q>7,\ c=7\text{: } (P_{1+c}+P_{7+c}):(P_{2+c}+P_{6+c}) = (P_{2+c}+P_{6+c}):(P_{3+c}+P_{5+c}) = 1;$$

For the *d*-elements:

$$\text{for } q \leqslant 5,\ e=0\text{: } (P_{1+e}+P_{5+e}):P_{3+e} = (P_{2+e}+P_{4+e}):P_{3+e} = 2;$$
$$\text{for } q>5,\ e=5\text{: } (P_{1+e}+P_{5+e}):(P_{2+e}+P_{4+e}) = 1.$$

It is important to emphasise that these expressions relate the properties of different elements of the same series. For example, in the first half of a series, the ratio $(P_{1+c} + P_{7+c}):P_{4+c}$ is determined by the properties of the ions with the electron configurations $f^1(^2F)$, $f^7(^8S)$, and $f^4(^5I)$: the triply-charged ions of thorium, curium, and neptunium, or the quadruply-charged ions of protactinium, berkelium, plutonium, etc. These relationships are particularly useful for those elements whose properties are difficult to measure because they are available in only small quantities or are highly radioactive, etc.

For redox reactions in each half of a series, inversion of the normal term takes place relative to the element for which it does not change:

$$d^1 \rightarrow d^0 + e\text{: } D \rightarrow S;\quad d^5 \rightarrow d^4 + e\text{: } S \rightarrow D;$$
$$d^2 \rightarrow d^1 + e\text{: } F \rightarrow D;\quad d^4 \rightarrow d^3 + e\text{: } D \rightarrow F;$$
$$d^3 \rightarrow d^2 + e\text{: } F \rightarrow F.$$

For the elements of the *d*-, *f*-, *g*-, and *h*-series, these reactions are:

$$d^3 \rightarrow d^2 + e;\quad f^4 \rightarrow f^3;\quad g^5 \rightarrow g^4;\quad h^6 \rightarrow h^5$$
$$F \rightarrow F \qquad I \rightarrow I \qquad N \rightarrow N \qquad U \rightarrow U\,.$$

III. Experimental confirmation of the periodicity of the change in the properties of the free atoms and ions with change in the number of electrons

1. Excitation energies

For neutral atoms, the periodic character of the change in the excitation energies with change in the number of electrons $f^{q-1}ds^2 \rightarrow f^q ds$, $f^q ps$, $f^q s^2$, $f^q d^2$ has been noted in a number of studies.[2,4,9] The presence of the electrons in the *dsp*-atomic orbitals and the similarity in the energies of several electron configurations for the elements of the start of the actinide series, however, lead to slight departures from the predictions of periodicity theory. For lanthanide and actinide atoms in f^q-electron configurations, when the one-configuration approximation is sufficiently correct, the dependence of the excitation energies on q is close to the theoretical. This leads to the rule of intervals for the excitation energies (Table 1). For a comparison of the *p*-, *d*-, and *f*-elements, Fig. 3 gives various excitation energies calculated from spectral data.[5–8] They confirm the periodicity in the change in excitation energies, the existence of the plateau section for the *d*- and *f*-elements, and its absence for the *p*-elements. In addition, the experimental values of the excitation energies E for the doubly-charged ions of the $3d$-series,[5] $3d^q \rightarrow 3d^{q-1}4s$, satisfy the relationships

$$[E\,(\text{Ti}) + E\,(\text{Gr})]/E\,(\text{V}) = 1.99;\quad [E\,(\text{Fe}) + E\,(\text{Zn})]/E\,(\text{Ni}) = 2.00;$$
$$[E\,(\text{Co}) + E\,(\text{Cu})]/E\,(\text{Ni}) = 1.99,$$

confirming the applicability of the rule of intervals for these ions.

The excitation energies of the free atoms and ions correlate with many properties of their compounds:[10–13] redox potentials, energy of cohesion of the metals, and thermodynamic stability; these properties determine the semiconducting, superconducting, and magnetic properties, etc. In the chemistry of the lanthanides and actinides, the solution of the problem of the localisation or delocalisation of electrons is related primarily to the question of the excitation of the electrons and their transfer to an unoccupied *d*-level. This range of problems makes it important to study the regularities of the change in the excitation energies with change in the atomic number of the elements.

2. Ionisation potentials

Jørgensen[11] expressed the ionisation energy of *f*-electrons in terms of the parameter V defining the reference point, the energy of stabilisation of the *f*-electrons from one element to another $E - A$, the spin–orbit splitting energy ζ, and the parameter D, defined as a linear combination of Slater–Condon integrals:†

$$q=1\text{: } I_1 = V + 2\zeta;\quad q=2\text{: } I_2 = V + (E-A) + (^8/_{13})D + 9E^3 + \zeta;$$
$$q=3\text{: } I_3 = V + 2(E-A) + (^{16}/_{13})D + 12E^3 + {}^1/_2\zeta;$$
$$q=4\text{: } I_4 = V + 3(E-A) + (^{24}/_{13})D;$$
$$q=5\text{: } I_5 = V + 4(E-A) + (^{32}/_{13})D - 12E^3 - {}^1/_2\zeta;$$
$$q=6\text{: } I_6 = V + 5(E-A) + (^{40}/_{13})D - 9E^3 - \zeta;$$
$$q=7\text{: } I_7 = V + 6(E-A) + (^{48}/_{13})D - 2E^3 - 2\zeta;$$
$$q=8\text{: } I_8 = V + 7(E-A) + (^{48}/_{13})D + {}^3/_2\zeta,$$
$$q=9\text{: } I_9 = V + 8(E-A) + (^{40}/_{13})D + 9E^3;$$
$$q=10\text{: } I_{10} = V + 9(E-A) + (^{32}/_{13})D + 12E^3 + {}^1/_2\zeta;$$
$$q=11\text{: } I_{11} = V + 10(E-A) + (^{24}/_{13})D;$$
$$q=12\text{: } I_{12} = V + 11(E-A) + (^{16}/_{13})D + 21E^3 - {}^1/_2\zeta.$$

† Jørgensen[11] gives estimates of the parameters used for the Ln^{3+} ions: $E - A \simeq 3000$ cm^{-1}, $D \simeq 6500$ cm^{-1}; the values of ξ change from 650 cm^{-1} to 2950 cm^{-1} on going from Ce^{3+} to Yb^{3+}. In the examination of the relative change in the ionisation potentials in the *f*-series, the values of the one-electron energies V are excluded.

Table 1. Change in the excitation energies[7,8] illustrating the rule of intervals.[1,2,13]

No.*	$(f^x+f^y):f^{(x+y/2)}$	An^{2+}			An^{3+}			Ln^{3+}			Ln^{3+}		
		6d	7s	7p	6d	7s	7p	5d	6s	6p	5d	6s	6p
1	$(f^1+f^7):f^4$			1.88	2.03	1.92	1.96	1.98	1.92	1 93	1.98	1.97	1.96
2	$(f^2+f^6):f^4$			1.96	1.95	1.97	1.98	1.93	1.98	1.98	1.99	1.99	1 99
3	$(f^3+f^5):f^4$			1.98	1.98	1.99	2.00	1.98	2.00	2.00	2.00	2.00	2.00
4	$(f^8+f^{14}):f^{11}$	1.90	1.84	1.95	1.95	1.96	1.97	1.84	1.97	1 90	1.97	1.99	1.97
5	$(f^9+f^{13}):f^{11}$	1.95	1.92	1.98	1.98	1.98	1.99	1.89	1.98	1.97	1.98	1.99	1.99
6	$(f^{10}+f^{12}):f^{11}$	1.99	1.98	2.01	1.99	1.99	2.00	1.98	1.99	1.98	1.99	1.99	2.00
7	$(f^1+f^7):(f^2+f^6)$			1.04	1.00	0.97	1.01	1.01	1.02	0.98	1.00	0.99	1.00
8	$(f^2+f^6):(f^3+f^5)$			1.02	0.98	1.01	1.01	1.02	1.02	1.04	1.01	1.00	1.00
9	$(f^8+f^{14}):(f^9+f^{18})$	0.97	1.04	1.01	0.99	0.99	0.95	0.97	0.99	0.96	1.01	0.99	1.00
10	$(f^9+f^{13}):(f^{10}+f^{12})$	1.00	1.03	0.98	1.01	1.01	1.00	1.02	1.00	1.01	1.01	1.00	1.00

* The theoretical values are 2.00 for ratios 1–6, and 1.0 for ratios 7–10.

From these expressions it follows that

$(I_1 + I_7) : I_4 = (I_2 + I_6) : I_4 = (I_3 + I_5) : I_4 = (I_8 + I_{14}) : I_{11} = (I_9 + I_{13}) : I_{11} = (I_{10} + I_{12}) : I_{11} = 2.00$.

Table 2 gives the corresponding relationships for the doubly- and triply-charged lanthanides and actinides.

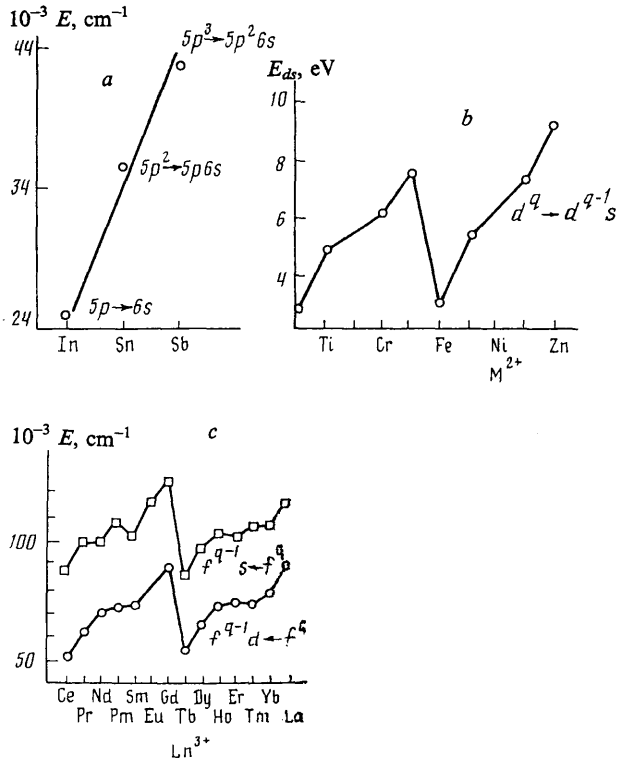


Figure 3. Excitation energies for elements of the *p*- (*a*), *d*- (*b*), and *f*-series (*c*): $p^q \rightarrow p^{q-1}s$; $d^q \rightarrow d^{q-1}s$; $f^q \rightarrow f^{q-1}s$.

3. Redox potentials

Fig. 4 illustrates the periodicity of the change in the oxidation potentials for $E^0(An^{2+}/An^{3+})$, $E^0(Ln^{3+}/Ln^{4+})$, and $E^0(An^{4+}/An^{5+})$, which have been measured or calculated. The general trends in the change in the potentials $E^0(An^{+}/An^{2+})$, $E^0(An^{2+}/An^{3+})$... for the actinides are shown in Fig. 5, from which it can be seen that the numbers of the atoms corresponding to the so-called plateau section are displaced with change in the oxidation state. For example, for the actinides:

E^0(II/III) — Pa, U, Np;
E^0(III/IV) — U, Np, Pu;
E^0(IV/V) — Np, Pu, Am.

This displacement is characteristic of the ranges corresponding to the sharp and sharpest changes in the properties in both series, lanthanides and actinides.

Table 2. Change in the ionisation potentials of the lanthanides[12] and actinides[13] illustrating the rule of intervals.[1,2,13]

Ratio of the ionisation potentials	Ln^{2+}	Ln^{3+}	Ln^{4+}	An^{2+}	An^{3+}
$(f^1+f^7):f^4$	1.99	1.97	1.98	2.065	1 95
$(f^2+f^6):f^4$	1.97	1.99	1.99	2.09	2.00
$(f^3+f^5):f^4$	1.98	2.02	1.99	2.035	2.00
$(f^8+f^{14}):f^{11}$	2.00	1.99	1.99	2.00	1.99
$(f^9+f^{13}):f^{11}$	1.99	1.99	1.99	2.045	1.99
$(f^{10}+f^{12}):f^{11}$	1.99	1.99	1.99	1.99	1.99
$(f^1+f^7):(f^2+f^6)$	1.01	1.02	1.00	0.99	0.97
$(f^2+f^6):(f^3+f^5)$	0.99	1.00	1.01	0.97	1.00
$(f^8+f^{14}):(f^9+f^{13})$	0.99	0.99	0.99	0.99	0.99
$(f^9+f^{13}):(f^{10}+f^{12})$	1.00	1.00	1.00	1.00	1.00

IV. Thermodynamic properties of compounds of the *f*-elements

1. Hydrated ions

The chemistry of aqueous solutions, and allowance for the influence of hydration on the physical and chemical properties of ions, represent an extensive and varied problem. Water is a strongly polar solvent, in which both cations and anions are solvated, and in which even the hydrated electron may be formed. The effects of lanthanide and actinide ion hydration have been studied by a number of authors.[15–17] In particular, the solubility, conductivity, relative viscosity, free energies of hydration, and equilibrium constants of aqueous solutions of lanthanide salts, etc. have been measured.

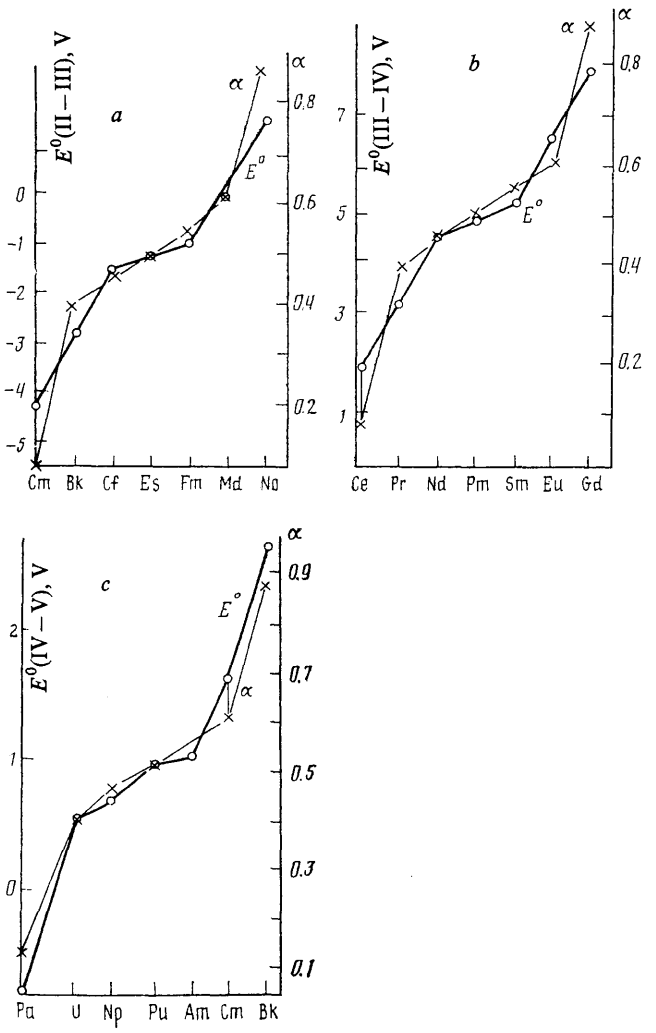


Figure 4. Periodicity of the change in the redox potentials in the lanthanide and actinide series.

The behaviour of lanthanide and actinide ions in solution is characterised by a number of specific features. Thus in aqueous solutions the dependence of the thermodynamic and transport properties on the number of electrons is regular for the light ions from La to Nd and the heavy ions from Tb to Lu, whereas the properties change in the opposite sense for the ions from Pm to Gd. This unusual behaviour for the *f*-series is due to the nature of the interaction of the *f*-ions with water molecules and the change in the coordination number of the lanthanides with change in the number of electrons of the ion. Similar studies were later carried out for actinide ions.[16] The electronic structures of the hydrated ions have been calculated.[18] All these experimental and theoretical studies show that the chemical bonds in the hydrated ions are partly covalent, as revealed by a variety of physicochemical properties. The important role of the second coordination sphere in hydration in different solutions has been revealed. Although the problem of the aqueous solutions of the lanthanides and actinides is complex and varied, a number of general semi-empirical and empirical relationships in the structures of the hydrated ions and the thermodynamic properties are firmly established (Fig. 6).

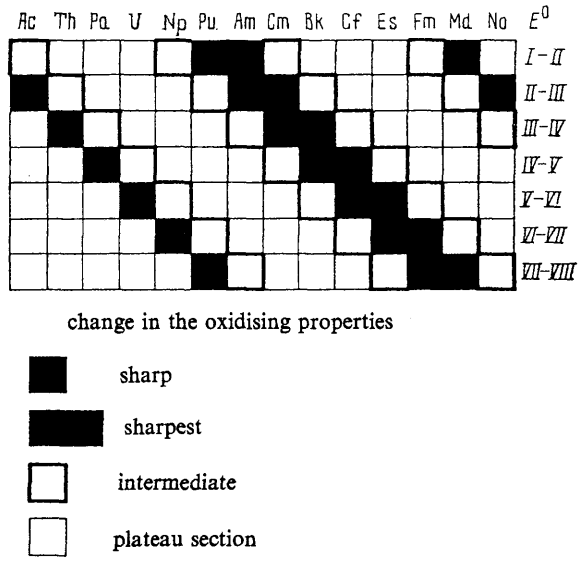


Figure 5. Diagram of the change in the oxidising properties of the actinides.

With increase in the number of electrons q in the f^q-electron configurations, the partial molar volumes $\overline{V}^0_m$ decrease for the light lanthanides (f^0–f^4), increase for the elements of the middle of the series (f^5–f^8), and decrease again for the heavy lanthanides (f^9–f^{14}) (Fig. 6*a*); that is, there are three clearly defined regions of change in $\overline{V}^0_m$.

The total number of water molecules h surrounding the ion, and the number of water molecules n_m in the first hydration shell, change in the opposite sense with increase in the number of electrons q for both series (Ln and An). The curves giving the dependence of h and

n_m on q show two plateaux for the light and heavy elements. A crossed analogy is observed for the lanthanides and actinides: a short plateau section for the light lanthanides and heavy actinides, and a long plateau section for the heavy lanthanides and the light actinides (Figs. 6*b* and 6*c*).

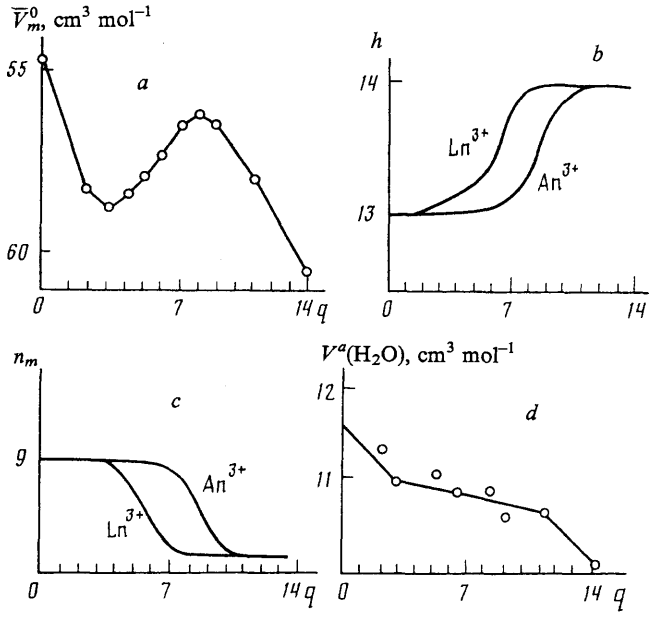


Figure 6. The three types of dependence of the properties of the triply-charged lanthanide and actinide ions in solution on the number of electrons: *a*, partial molar volumes; *b*, number of water molecules in the first and second hydrate layers; *c*, number of water molecules in the first hydrate layer; *d*, average volume of a bound water molecule in the hydrate layer.

The sections of intermediate change in h and n_m in the lanthanides and actinides are displaced: for the lanthanides this section lies in the first half of the series (Pr, Sm, Eu, and Gd), and for the actinides it lies in the second half (Cm, Bk, Cf) (Figs. 6*b* and 6*c*).

The average volume of the water molecules in the hydration shell (Fig. 6*d*) decreases with increase in the number of electrons q; a sharp decrease in volume is observed at the beginning and end of the series, and a plateau in the middle.

The thermodynamic properties of the aquo-ions have been analysed.[19] The enthalpy of hydration H_h for Ln^{3+} and An^{3+} changes regularly and almost linearly along the series, except for the elements in the middle of the series. The components of H_h, however, that is the enthalpy of formation of the aquo-ions $H(Ln^{3+}_{aq})$ and the cations $H[Ln^{3+}(gas)]$ change irregularly and in opposite directions, due to the existence of the compensation effect. As a result, the dependence of H_h on q for Ln^{3+} and An^{3+} is close to linear. This makes it possible to calculate the quantity $H_h(An^{3+})$ using approximate equations, for example:[20]

$$H_h = \frac{7.32Z^2(An^{3+})}{R+0.85},$$

where R is the radius of the ion with charge Z, and the constant 0.85 characterises the change in the radius of the ion in solution.

2. Halogen compounds of divalent and trivalent lanthanides and actinides

Since the halogen compounds of the lanthanides and actinides have important practical applications, their properties, in particular their thermodynamic properties, have been studied by many authors, by both experimental[21–24] and theoretical[25,26] methods. The enthalpies of formation of $LnHal_3$ have been determined by mass spectrometry, solution calorimetry, etc., and also calculated from the equation

$$H_0[MX(crystalline)] = H_0[M^{Z+}(gas)] + \frac{A}{R_{M^{Z+}} + R_X} + B,$$

$$H_0[M^{Z+}(gas)] = H_{sub}(M) + \sum_{i=1}^{3} I_i + {}^5/_2 ZRT,$$

where $R_{M^{Z+}}$ is the ionic radius of the metal, R_X the radius of the anion, A and B are constants, $H_{sub}(M)$ the standard enthalpy of sublimation, and $\sum_{i=1}^{3} I_i$ the sum of the ionisation energies; the last term represents the change in enthalpy as a function of temperature for an ideal gas.

According to published data,[25,26] the enthalpy of formation of $LnHal_3$ shows an irregular dependence on the number of f-electrons. In addition to the features of the structure of the f-levels characteristic of Ln^{3+}, revealed by the change in the values of H_{sub} and $\sum_{i=1}^{3} I_i$, the irregular change in $H_0(LnHal_3)$ with change in the number of f-electrons is also related to a change in the type of crystal structure. Thus in the trifluorides, the tetragonal LaF_3 structure is replaced in the second half of the series by the hexagonal–trigonal α-YF_3 structure. At the same time there is a change in the coordination number of the metal: with increase in the number of electrons q for the $Ln^{3+}(f^q)$ ion, the ninth fluorine atom is, as it were, displaced from the first coordination sphere, so that, for example, for HoF_3 and YbF_3 the internuclear distance Ln–F for one of the nine fluorine atoms is greater by 0.20 Å and 0.34 Å respectively[27] than the average Ln–F distance for the other eight fluorine atoms. This effect is similar to that observed for the aquo-ions, where the number of water molecules in the first coordination sphere changes from nine to eight on going from the ions of the light elements to the ions of the heavy elements.

At all stages of the development of the theory of the compounds of the trivalent f-elements, new examples of chemical regularities have been discovered. These regularities show a common feature, however, namely a regular change in properties for the light and heavy elements, and an anomalous change for the intermediate elements. The section of the anomalous relationship may include a larger or smaller number of elements, depending on the type of ligand, but for these elements there is always a change in the coordination number, internuclear distances, structure, etc.

The existence of three regions of change in the crystal-chemical properties is reflected in the melting points T_f and the enthalpies of solution. Thus the compounds LnF_3 can be divided into three groups, depending on the values of T_f: the heavy Dy–Lu, the light La–Nd, and the intermediate Nd–Dy.[28]

The difference between the lattice enthalpy of a crystalline compound H_c and the enthalpy of hydration of the ionic components determines the enthalpy of solution H_s. For $LnHal_3$,[21] the change in structure, for example for $EuF_3 \rightarrow GdF_3$ or $GdCl_3 \rightarrow TbCl_3$, is due to the anomalous change in H_s.

The experimental values of H_c are known for the chlorides of the actinides of the middle of the series:[21] for UF_3, H_c = −1502 kJ mol^{-1}, and for PuF_3, H_c = −1586 kJ mol^{-1}; for the chlorides of uranium, plutonium, americium, and curium, the corresponding values are −866, −960, −978, and −974 kJ mol^{-1}; for the bromides of uranium, neptunium, and plutonium, H_c = −699, −730, and −793 kJ mol^{-1}; and for the iodides of these metals, H_c = −467, −513, and −580 kJ mol^{-1} respectively. Solution calorimetry has been used to measure the standard enthalpies of formation of $CsSmCl_3$, $CsTmCl_3$, and $CsYbCl_3$.[29] The last two compounds have the ideal perovskite structure, and $CsSmCl_3$ and $CsEuCl_3$ have a distorted perovskite structure. The experimental values of H_0 for the synthesised compounds $CsLnCl_3$ and the calculated values for $CsNdCl_3$ and $CsDyCl_3$ correlate with the corresponding values for $LnCl_3$:

Ln in $CsLnCl_3$	Nd	Sm	Dy	Tm	Yb
H_0, kJ mol^{-1}	−1124	−1230	−1165	−1194	−1285

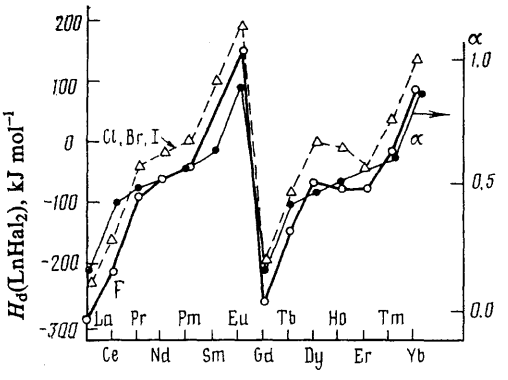


Figure 7. Dependence of the parameter α and the free enthalpies of decomposition (H_d) according to the scheme $LnHal_2 \rightarrow {}^1/_3Ln + {}^2/_3LnHal_3$ on the atomic number of the element.

The standard enthalpies of formation of the corresponding compounds $LnHal_2$ and $LnHal_3$, and also $AnHal_2$ and $AnHal_3$, can be used to calculate the standard enthalpies of the disproportionation

$$MHal_2 \rightarrow {}^1/_3M + {}^2/_3MHal_3$$

where M = Ln or An. The principal quantity determining the nature of the change in the enthalpies of decomposition with change in atomic number is not the sum of the ionisation potentials, as in the case of the enthalpies of formation, but the difference in the sums of the ionisation potentials, that is the third ionisation potential. This leads to a periodic change in the values of the enthalpies of decomposition in accordance with the periodic change in the ionisation potentials and the parameter α. This leads to the characteristic dependence of the enthalpies of decomposition on the number of electrons (Figs. 7 and 8).

3. Halogen compounds of tetravalent lanthanides and actinides

Experimental studies of the thermodynamic characteristics of the tetrafluorides are limited to the mass-spectral analysis of TbF_4 and CeF_4, tensimetric measurements for CeF_4, PrF_4, and TbF_4, and calorimetric measurements for CeF_4 and TbF_4 in an HCl + H_3BO_3 mixture.[24] The experimental values of $H_0(LnF_4)$ show a large scatter.

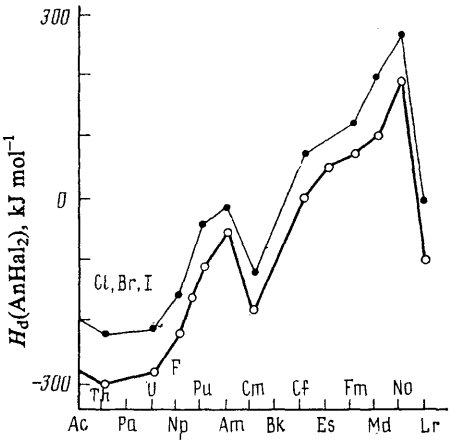


Figure 8. Dependence of the standard enthalpies of decomposition (H_d) according to the scheme $AnHal_2 \rightarrow {}^1/_3An + {}^2/_3AnHal_3$ on the atomic number of the element.

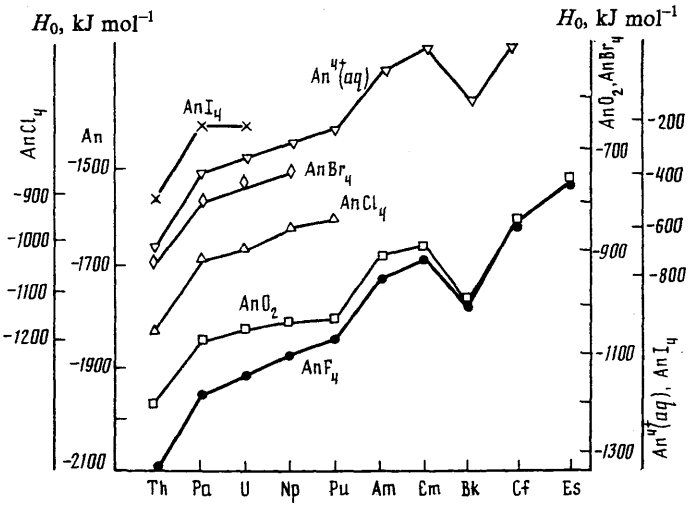


Figure 9. Dependence of the standard enthalpies of formation on the atomic number of the element.

The thermodynamic properties of the actinide tetrahalides ThF_4, PaF_4, UF_4, NpF_4, PuF_4, and AmF_4 have been studied experimentally.[21] Even for thorium tetrafluoride, however, the standard enthalpies of formation measured in fourteen studies show a scatter in the values of about 36 kJ mol^{-1}. Fig. 9 gives the dependence of the measured and calculated enthalpies of formation of the actinide tetrahalides in solution on the number of *f*-electrons. The data for

AnO_2 and $An^{4+}(aq)$ [21] are given for comparison. A noteworthy feature is the clearly defined plateau for Pa(f^1), U(f^2), Np(f^3), and Pu(f^4) and the sharp change in the enthalpies of formation on going from Th(f^0) to Pa(f^1) and from Pu(f^4) to Am(f^5) in the first half of the series. The same characteristics are observed for the compounds of the lanthanides.

The values of the enthalpy of decomposition of the tetrahalides

$$MHal_4 \rightarrow Hal + MHal_3$$

are determined by the difference

$$\sum_{i=1}^{4} I_i - \sum_{i=1}^{3} I_i.$$

Thus the rule of intervals formulated above is also applicable in this case.

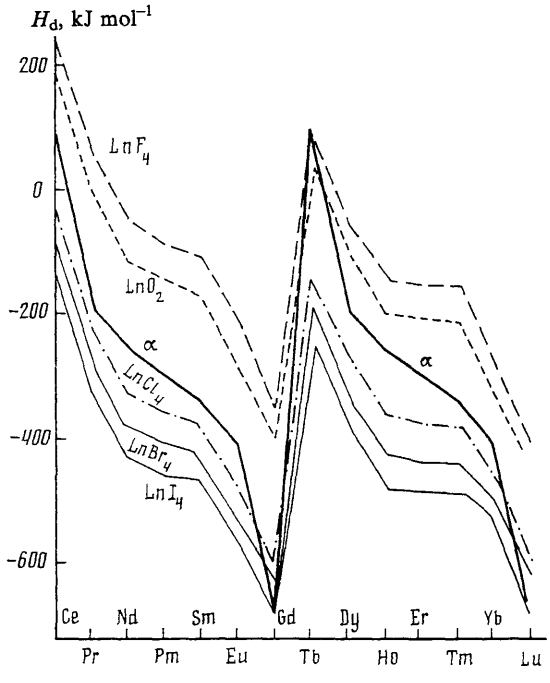


Figure 10. Dependence of the standard enthalpies of decomposition according to the scheme $LnX_4 \rightarrow X + LnX_3$ on the atomic number of Ln.

4. Oxides and chalcogenides

Of the lanthanide monoxides, EuO and impurity YbO have been characterised; in the monoxides LaO, CeO, PrO, NdO, and SmO, two valence electrons from the lanthanide atom are used for chemical bond formation, and the third for the formation of the conductivity band. Monoxides of Th, U, Np, Pu, and Am, formed on the surface of the metals, are known. The monoxide PuO is also obtained by reducing the dioxide PuO_2 using Pu and C; AmO is formed by the reaction of Am with HgO or in the gas phase. The standard enthalpies of formation of LnO and AnO have been calculated.[25,26]

For various lanthanides existing in the divalent state, for example La, Ce, Gd, and Lu, the one-configuration approximation is inadequate, and it is necessary to take account of several electron configurations involving *d*- or *s*-orbitals: $f^q + f^{q-1}d + f^{q-1}s \ldots$ In this case the rule of intervals for the disproportionation $MO \rightarrow {}^1/_3M + {}^2/_3MO_{1.5}$ should not apply. If however the electron configuration of the lanthanide f^q in the divalent state is stable, the rule of intervals applies.

In Fig. 10 the standard enthalpies of the decomposition $LnO_2 \rightarrow {}^1/_2O + LnO_{1.5}$ are compared with the corresponding values for $LnHal_4$. The characteristic periodicity of the change in these values with change in the number of electrons is again observed. Irrespective of the ligands, for all compounds of the tetravalent lanthanides and actinides, the standard enthalpies of decomposition change in accordance with the theoretical dependence of α on *q*. This periodicity should also be observed for higher oxidation states, for example for An_2O_5 (An = Pa, U, Np, Pu, ...), where the series includes hypothetical compounds.

For the sulphides and pnictides of the lanthanides and actinides, according to calculations of the standard enthalpies of formation of MS, $MS_{1.5}$, MS_2, and MAs, where M = Ln or An,[25,26] the same trends are observed in the change in these quantities with increase in the atomic number as in the case of the corresponding oxides, that is for the systems MO and MS, $MO_{1.5}$ and $MS_{1.5}$, and MO_2 and MS_2. An analogy is also observed in the dependence of the standard enthalpies of decomposition to the metal and the corresponding sulphide on the number of electrons.

V. Metals of the *d*- and *f*-series and intermetallic compounds

1. Crystal structures and electron configurations

Fundamental studies of the metallic lanthanides and actinides have been carried out in recent years, and the results reviewed.[30–35] In these studies, the role of the 4*f*- and 5*f*-electrons in the formation of the metallic bond was extensively discussed. Many problems have been resolved, but there is still no answer to the main question, namely the actual electron configurations of the atoms in the metals and the oxidation states of various actinides in the metals.

In accordance with the main purpose of the present review, which is to follow the regularity in the change in various properties of the lanthanides, actinides, and their compounds and to compare them with other series of elements, this task will also be carried out for the *d*- and *f*-metals.

In the lanthanide series, all the metals are trivalent, except Eu and Yb, and in the actinide series the heavy elements are divalent in the metallic state, the light actinides include tetravalent metals, and the intermediate elements are trivalent. In the actinide series, anomalous effects associated with a change in oxidation state will be superimposed on the periodicity in the change in properties due to the structure of the 5*f*-level.

The light metallic actinides (as far as plutonium) have crystal structures with a low symmetry; for plutonium, six different phases exist in the temperature range from 298 K to 913 K. Distorted and complex structures are generally formed if the 5*f*-electrons are involved in the production of the metallic band. The crystal structures of the heavy metals resemble the structures of the metallic lanthanides. The crystal structures are different for the light and

heavy actinides. The largest number of phases is observed for the metals in the middle of the series.

The crystal structure depends on the energy of excitation from the electron configurations of the ground state into low-lying excited states. Thus in the lanthanide series, where the 4*f*-electrons remain practically non-bonding, the crystal structure is determined by the valence *d*- and *s*-electrons, that is by the electron configurations: $f^q ds^2$, $f^q d^2 s$, $f^q dsp$, $f^{q+1} s^2$, $f^{q+1} ds$, $f^{q+1} sp$. If the neutral atom has the electron configuration $f^q ds^2$, then in the metal with the double hexagonal structure its electron configuration changes from $f^q d^{1.3} sp^{0.7}$ to $f^q d^{0.9} sp^{1.1}$.[33] If in the free state the atom has the electron configuration $f^{q+1} s^2$, then in the metal with the double hexagonal structure it changes from $f^{q+1} d^{0.3} sp^{0.7}$ to $f^{q+1} sp$.

2. Melting points of the metallic actinides

The change in the melting point T_f in the series of metallic actinides reflects their complex electronic structure. On going from metallic thorium to einsteinium, T_f changes from 2023 K to 1133 K. Even for metals having delocalised 5*f*-electrons, such as Pa, U, Np, and Pu, the melting point changes from 1840 K to 913 K. The dependence of T_f on the atomic number of the element is shown in Fig. 11. At high temperatures close to the corresponding melting points, the heavy metals (from Am to Es) have a face-centred cubic structure, and the light actinides (from Th to Np) a body-centred cubic structure.

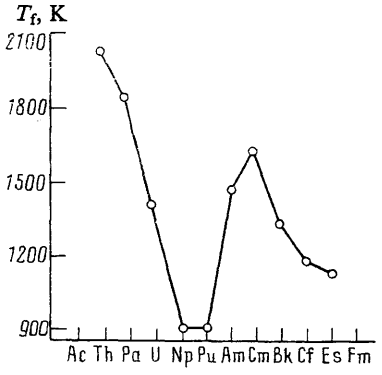


Figure 11. Dependence of the melting points of the metallic actinides on the atomic number.

The melting point T_f of the metal depends on the atomic number of the element. It decreases on going from Th to Np and Pu, increases from Pu to Am, and then decreases regularly from Cm to Fm. There is a correlation between the T_f values and the orbital quantum numbers L_q of the normal terms of the actinide ions: Th(f^0), Np(f^3), Pu(f^4), Am (f^6), Cm(f^7), Bk(f^8) (Fig. 12). These electron configurations correspond to the tetravalent states for the light actinides (from Th to Pu), the trivalent states for the elements of the middle of the series (from Bk to Am), and to divalent states for the heavy actinides (from Es to No).

The populations of the valence orbitals in the metals are fractional. The values for the 5*f*-orbitals are apparently greater than those indicated above. Fig. 12 shows clearly that the electron configurations Th(f^0), Np(f^3), Pu(f^4), Am(f^6), Cm(f^7), and Bk(f^8) have a significant influence on the production of the electronic structure of the atoms in the metals.

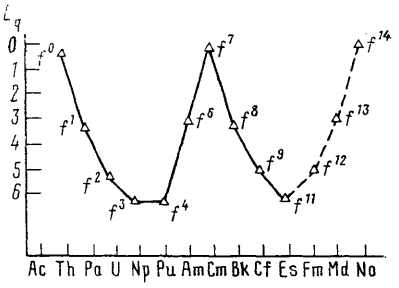


Figure 12. Change in the orbital quantum numbers L_q of the normal terms of the actinide ions with change in q.

3. Bond lengths in the metals and atomic volumes

The bond lengths in metals are fundamental characteristics and determine many of their properties—atomic volumes, band width, bond strength, etc. Data on the dependence of the atomic radii on the atomic number of the element have been compared for the metals of the *d*-series and the actinides.[31] For the metals of the 3*d*-series, the dependence is close to parabolic, and shows a double–double effect similar to that observed for the ionic radii in various compounds of these elements. This effect is revealed more clearly for the metals of the 3*d*-series than for the metals of the 4*d*- and 5*d*-series, since the 3*d*-electrons are more localised.

The almost parabolic dependence of the metallic radii on the atomic number is responsible for the same behaviour of the atomic volumes of the metals of the *d*-series.

The lanthanides Eu and Yb show anomalous values of the atomic volumes. This is related to the fact that Eu and Yb are divalent. From the corresponding relationship for the atomic volumes of the metallic actinides it was concluded[35] that the light actinides (from Th to Pu) are tetravalent.

4. Energies of cohesion

a) Metals of the *d*-series

The change in the energy of cohesion E_c for the metals of the 3*d*-series[35] is described by a curve which is close to parabolic, with a minimum at the middle of the series. The parabolic relationship breaks down for metallic manganese, although significant anomalies are not observed for the manganese analogues technetium and rhenium.

Among the metals of the 3*d*-series, Ca, Ni, and Cu have a face-centred cubic structure, Sc, Ti, and Co a double hexagonal structure, and V, Cr, and Fe a body-centred cubic structure; metallic manganese has a complex crystal structure with several non-equivalent atoms in the cell. The metals of the 4*d*-series have different crystal structures: Sr, Rh, Pd, Ag have a face-centred cubic structure; Ru and Cd a double hexagonal structure; and Nb and Mo a body-centred cubic structure. In these crystals, the metal atoms have the electron configurations $d^{q-x} sp^x$ and $d^q s$; the

contribution of the *p*-orbitals is greater for the double hexagonal system than for the face-centred or body-centred cubic structures.

Spectroscopic data[5] can be used to estimate the sum of the energies of excitation from the electron configurations $3d^q4s^2$ of the ground state of the neutral atoms Sc, Ti, V, Mn, Fe, Co, and Ni into the electron configurations $3d^{q+1}4s$ and $3d^{q+1}4s4p$. Since in the ground state the Cr and Cu atoms have the electron configurations d^5s and $d^{10}s$ respectively, for these elements it is possible to take account of only the excitation into the electron configurations d^5p and $d^{10}p$. For the calcium atom, account was taken of the sum of the excitation energies $4s^2 \rightarrow 4s4p + 4s3d$, and for the zinc atom only the energy of the single excitation $4s^2 \rightarrow 4s4p$ was considered.

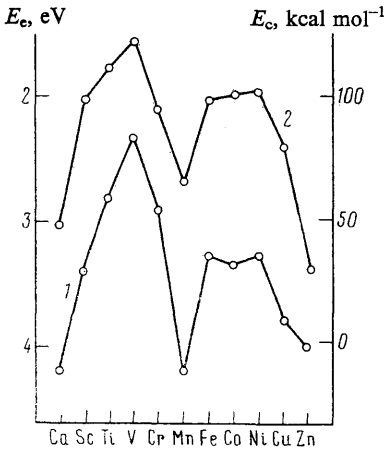


Figure 13. Correlation between the energy of cohesion of the metals and the sum of the energies of excitation from the electron configuration of the ground state d^qs^2 (Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Zn) and d^qs (Cr, Cu) into the electron configurations d^qsp and d^qs; for each excited electron configuration, the multiplet of lowest energy is used.

It is obvious that the greater the excitation energy (E_e) corresponding to the electron configuration of a given type of crystal lattice, the lower the energy of cohesion, that is an inverse relationship exists between these quantities. The sum of the excitation energies reflects completely the energies of cohesion of the metals of the 3*d*-series (Fig. 13). The existence of the plateau section on the graph giving the dependence of E_c on the atomic number for metallic Fe, Co, and Ni (Fig. 13) is due to the opposed trends in the change in the excitation energies of the free atoms. The values of the energies of excitation from the electron configurations of the ground state d^qs^2: Fe(d^6s^2, ^5D), Co(d^7s^2, ^4F), and Ni(d^8s^2, ^3F), into the electron configurations $d^{q+1}s$ and d^qsp can be considered. These values (in eV), together with the electron configurations and their terms, are given below:

	$3d^{q+1}4s$	$3d^q4s4p$
Fe (d^6s^2; ^5D):	2.4 ($^5F_5$);	0.86 ($^7D_5$)
Co (d^7s^2, ^4F):	2,93 ($^4F_{9/2}$);	0.43 ($^6F_{11/2}$)
Ni (d^8s^2, ^3F):	3.44 ($^3D_4$);	0.03 ($^5D_4$) .

The sums of these quantities differ little, leading to similar values of the excitation energy for the atoms and approximately equal energies of cohesion for these metals. Thus the properties of the free atoms correlate well with the properties of the metals; this applies both to the energies of cohesion and the moduli of compression of the metals (Fig. 14). Thus the relationship between the corresponding energies of excitation and energies of cohesion or moduli of compression is apparently close to linear.

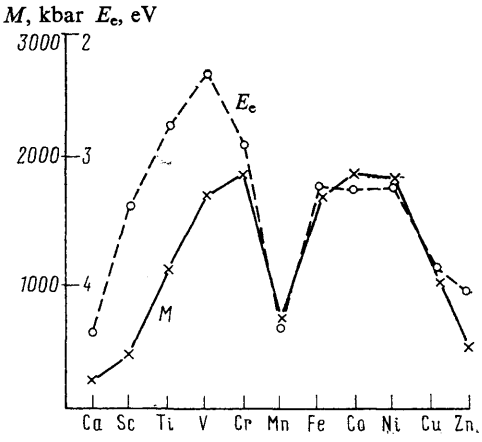


Figure 14. Correlation between the modulus of compression (M) for the metals of the 3*d*-series and the energies of excitation (E_c) into the hybrid state.

b) Metallic actinides

The dependence of E_c for the metallic actinides on the excitation energies has been studied.[33–36] Account was taken of the excitation energies[7,8] $f^qs^2 \rightarrow f^{q-1}ds^2$ and $f^{q-1}ds^2 \rightarrow f^{q-2}d^2s^2$ on going from the divalent to the trivalent and then to the tetravalent state. From this approach it was concluded[36] that Am, Cm, and Bk are trivalent. The valence of Cf is intermediate between 2 and 3, and the heavy metallic actinides, beginning with einsteinium, are divalent. For metallic Np and Pu, the picture is more complex and indefinite. From estimates of the excitation energies $f^{q-1}ds^2 \rightarrow f^{q-2}d^2s^2$ it follows that Np and Pu in the metallic state are apparently trivalent, but estimates of the atomic volumes and other properties indicate that they are tetravalent.

If for the light actinides (from thorium to plutonium) account is taken of the energies of excitation into the formally tetravalent states, accompanied by unpairing of the $7s^2$ electron pair, $f^{q-2}d^3s$ and $f^{q-2}d^2sp$, then the nature of the change in the excitation energy for Np, Pu, and Am will not reflect even the trend in the change in E_c. If however it is assumed that the hybrid functions in the metallic state are complex and are formed from several electron configurations: $f^{q-1}d^2s + f^{q-1}dsp + f^{q-2}d^3s + f^{q-2}d^2sp$, and that the contribution of the last two electron configurations is small, then it is possible to obtain not only a qualitatively correct description but also a quantitative description of the dependence of E_c on the excitation energy. In the second half of the series, the values of the energy of cohesion correlate with the energies of

excitation into both the divalent and the trivalent states. If it is assumed that Bk and Cf are trivalent in the metallic state, and that all the actinides from einsteinium onwards are divalent, the energies of cohesion of the metallic forms of these elements again do not agree with the experimental data. For the berkelium atom, the energies of excitation into the formal divalent and trivalent states are approximately equal. Thus the metallic state apparently corresponds to several electron configurations: f^8d^2s, f^8dsp, f^9sp.

Thus for the heavy metallic actinides, the change from Cm^{III} to No^{II} takes place in stages. To conclude this section, it may be noted that in the interpretation of the properties of the actinides it is incorrect to take account of only one electron configuration for each valence state: f^qs^2 for An^{II}, $f^{q-1}ds^2$ for An^{III}, and $f^{q-2}d^2s^2$ for An^{IV}, with integral values of the populations of the *f*-, *d*-, and *s*-orbitals. On going from Th to Pu there is an increase in the energies of excitation into the electron configurations $f^{q-2}d^3s$, $f^{q-2}d^2sp$, and $f^{q-2}d^2s^2$, indicating a decrease in their contribution to the overall electron configuration in the metals. Similarly, in the second half of the series, there is a gradual decrease in the contribution of the electron configurations $f^{q-1}d^2s$ and $f^{q-1}ds^2$ to the electron configurations of the metals, and the contributions from the f^qsp- and f^qsd-electron configurations increase.

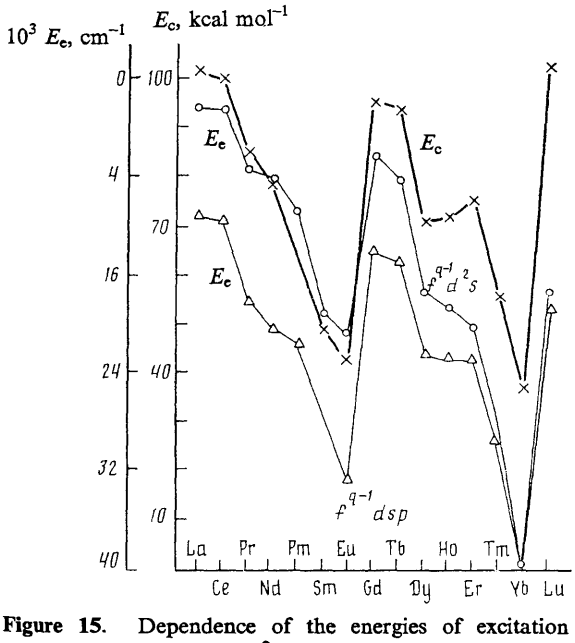


Figure 15. Dependence of the energies of excitation from the electron configuration f^qs^2 into the electron configurations $f^{q-1}d^2s$ and $f^{q-1}dsp$ on the atomic number of the element; in the first case the configurations $f^7ds + f^7d^2$ for Eu and $f^{14}ds + f^{14}d^2$ for Yb were used, and in the second case $f^7p^2 + f^7sp$, $f^7dp + f^7ds$ for Eu and $f^{14}ds + f^{14}dp$ for Yb; it can be seen that there is a correlation between the energies of excitation and cohesion E_c.

c) Metallic lanthanides

The dependence of the energy of cohesion of the metallic lanthanides on the atomic number reflects the periodicity in the properties of the free atoms more clearly than any other property. Fig. 15 gives the dependence of the energies of excitation from the electron configuration of the ground state f^qs^2 into the electron configurations $f^{q-1}d^2s$ and $f^{q-1}dsp$ for all the elements except Eu and Yb, for which the energies of excitation into the divalent states were used.[4] The changes in the energies of cohesion and in the energies of excitation with change in the atomic number show a remarkable similarity.

Comparison of the energies of cohesion for the metals of the *d*-series, the lanthanides, and the actinides shows that the atomic factor is preserved to the greatest extent for the metals of the 3*d*-series and the lanthanides, in accordance with the fact that the 4*f*-electrons are more localised than the 5*f*-electrons, and the 3*d*-electrons more localised than the 4*d*- and 5*d*-electrons.

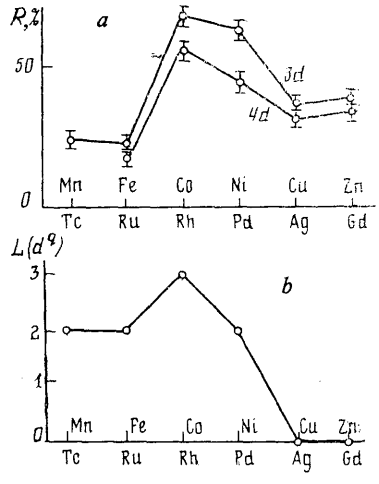


Figure 16. Ranges of change in composition (R) for the intermetallic compounds with metals M (*a*) and the dependence of the quantum numbers L for the electron configurations of the atoms M (*b*) in the metals ($d^qs^xp^y$) on the atomic number of M.

5. Intermetallic compounds of the lanthanides

The lanthanides form a large number of compounds with different compositions with the metals of the *s*-, *p*-, and *d*-series, and the regularities in the change in their properties can be followed. The most widely encountered compounds of the lanthanides with metals are the following: Ln_3M, Ln_5M_2, Ln_7M_5, Ln_9M_4, $Ln_{24}M_{11}$, Ln_2M, Ln_2M_{17}, Ln_5M_3, Ln_3M_2, Ln_4M_3, Ln_5M_4, $Ln_{11}M_{10}$, LnM, Ln_5M_{41}, Ln_6M_7, Ln_3M_4, Ln_7M_{10}, Ln_3M_5, LnM_2, LnM_3, Ln_2M_7, $Ln_{14}M_{51}$, Ln_3M_{11}, Ln_5M_{19}, Ln_6M_{23}, Ln_3M_{22}, LnM_4, Ln_4M_{17}, Ln_5M_{22}, $Ln_{13}M_{58}$, Ln_5M_{24}, LnM_5, LnM_6, LnM_7, LnM_{11}, LnM_{13}, LnM_{66}, etc. The relative concentration of Ln in the two-component compounds is restricted. The highest concentration of Ln in these compounds is apparently achieved in Ln_3M. The composition of the simplest compounds changes regularly for each system. These compounds are LnM_2 for the elements Mn, Tc, Re, and Fe, Ln_3M for the other transition elements, LnM for the elements of groups IB and IIB (except Au), and Ln_3M again for the elements of groups IIIA, IVA, and VA. A definite periodicity in the composition is observed. The most varied compositions with respect to M are shown by the compounds of the lanthanides with the group IIB

elements, whereas the elements from Al to Bi are characterised chiefly by the compounds LnM_3. Boron gives a large number of compounds with different compositions.

The composition of the compounds is determined chiefly by the electronic structure of M, that is by the number of *d*-, *s*-, and *p*-electrons for M. All the lanthanide compounds can be divided into three groups, depending on the electronic structure of M: 1) compounds with transition elements, 2) compounds with IB and IIB elements (except Au), and 3) all other compounds. If the range of change in the composition (R) of the compounds with respect to M is defined as the difference $R = R_u - R_l$, where R_u and R_l are the upper and lower percentage concentrations of M in the compounds with the highest and lowest concentrations of M, then an extremal value of R is reached in the middle of the second half of the series of *d*-elements (Fig. 16). This reveals a characteristic of the *d*-levels occupied to the extents of 1/2, 3/4, and 1, that is the values of R should correlate qualitatively with the values of the quantum numbers L_q for the normal term and the d^q-electron configurations corresponding to the hybridisation of the atoms in the pure metals: Mn, Tc (d^6s); Fe, Ru ($d^{6-x}p$); Co, Rh ($d^{8-x}sp^x$); Ni, Pd (d^9s); Cu, Ag ($d^{10-x}sp^x$); Zn, Cd ($d^{10}sp$).

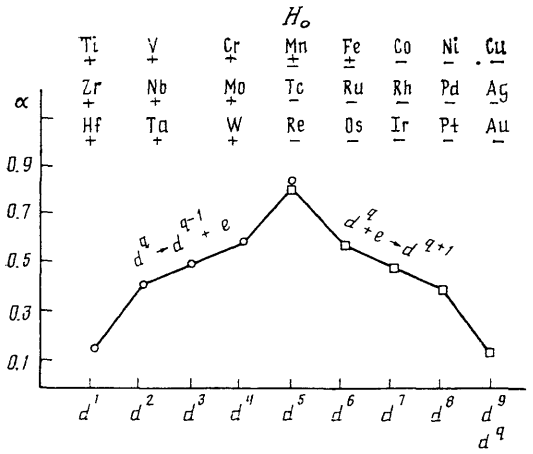


Figure 17. Dependence of α on q, showing that the most stable compounds of the 3*d*-metals with the lanthanides should be formed by the heavy 3*d*-metals; the upper part of the Figure gives the signs of the heats of formation of the compounds LnM.

The curve describing the dependence of the percentage concentration of the compounds LnM relative to the total number of compounds on the percentage concentration of M in the given type of compound is bell-shaped (the apex of the bell corresponds to the compounds LnM_2, the largest class of compound). The number of compounds with a given composition increases in the order: $Ln_5M_3 < LnM_3 < LnM < LnM_2$. In the reaction of the metals of the 5*d*-series and the lanthanides, the greatest bonding is achieved with the *d*-elements of the second half of the series. In their reaction with the elements of the first half of the 3*d*-series, the lanthanides should be reduced, and in their reaction with the elements of the second half they should be oxidised. Correspondingly, the 3*d*-elements in the first half of the series are oxidised, and those in the second half are reduced. The dependence on q of the values of $\alpha = [2L_{q+1} + 1][2L_{q+1} + 2L_q + 2]^{-1}$ for the first half of the series and $\alpha = [2L_{q-1} + 1][2L_{q-1} + 2L_q + 2]^{-1}$ for the second half determines the tendency to undergo oxidation on going from the d^5- to the d^1-electron configuration and to undergo reduction on going from the d^5- to the d^9-configuration. These trends are shown schematically in Fig. 17, which also gives the signs of the heats of formation of the intermetallic compounds H_0. The electron configuration d^5s^2 was used for all the *d*-elements.

The heavy *d*-elements act as electron acceptors $Ln^{\delta+}M^{\delta-}$, and the acceptor properties increase towards the end of the series (Fig. 17). The light *d*-elements should be electron donors, $Ln^{\delta-}M^{\delta+}$, and the donor properties should increase from the middle to the beginning of the series. Thus since they have a low electron affinity, the lanthanides should not tend to form intermetallic two-compounds with the light *d*-elements. The sign of the heat of formation is not always known for the middle of the series.

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The present review has analysed the general regularities in the change in the redox properties of the lanthanides, actinides, and elements of the *d*-series. This phenomenon is determined by the specific features of the electrostatic interaction of the *d*- or *f*-electrons. It leads to a characteristic change in the properties with increase in the number of electrons: a sharp–retarded–sharp change in each half of the series, and the sharpest change on going from one half of the series to the other.

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