Inorganica Chimica Acta, 94 (1984) 241–248

Lower Oxidation States of Lanthanides and Actinides

N. B. MIKHEEV

Institute of Physical Chemistry, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

Received October 5, 1983

Most lanthanides and all elements of the second half of the actinide family are known to have in a state of free neutral atoms the f^ns^2 electron configuration, which is analogous to the alkaline, earth elements having the $[s^2p^6]s^2$ structure. From this one can assume the basic oxidation state of the lanthanides and far actinides as being 2+. This is however only true in the case when the ionization energy of the double charged atom is substantially higher than the hydration (or solvation) energy difference between triple- and double charged ions of these elements. The basic oxidation state for the lanthanides and actinides, beginning with americium, is 3+ (except nobelium).

The divalent state of the lanthanides and actinides, according to our investigations [1], can be realized for all lanthanides from cerium to ytterbium and for all actinides from plutonium to nobelium. The stability of the divalent states of these elements differs depending on the standard oxidation potential $E^{\circ}_{M^{3+}/M^{2+}}$ (see Table I). As it is seen from Table I, the oxidation potentials for most elements coincide with those theoretically calculated by Nugent [2]. However, the experimental figures for cerium, gadolinium, therbium, plutonium, and curium turn out to be much higher than the calculated data. If based on the theoretically calculated values of $E^{\circ}_{M^{3+}/M^{2+}}$ for these elements we would come to the impossibiltiy of their reduction to the oxidation state 2+. Apart from our research [3, 4], the reduction of Ce^{3+} to Ce^{2+} has been described elsewhere [5], as has the reduction of Cm^{3+} to Cm^{2+} [6]. We were the first to establish the existence of Gd^{2+}, Tb^{2+} and Pu^{2+} [7, 8].

The standard oxidation potential $E^{\circ}_{M^{3+}/M^{2+}}$ is known to be determined by three factors: the energy of ionization of free double charged atoms $M^{2+} \rightarrow M^{3+} + e$ (ΔG°_{ion}), and the energies of hydration of

TABLE I. The Oxidation Potential Values $E_{M^{3+}/M^{2+}}{}^{\circ}$ for Lanthanides and Actinides.

Ln	$E^{\circ}_{Ln^{3+}/Ln^{2+}}$, V		An	$E^{\circ}_{An^{3+}/An^{2+}}$, V	
	Experimental Data	Data Calculated by Nugent [2]		Experimental Data	Data Calculated by Nugent [2]
La	it is unknown	−3.1 ± 0.2	Ac	it is unknown	−4.9 ± 0.2
Ce	−2.92 ± 0.08	−3.2 ± 0.2	Th	it is unknown	−4.9 ± 0.2
Pr	−2.84 ± 0.06	−2.7 ± 0.2	Pa	it is unknown	−4.7 ± 0.2
Nd	−2.62 ± 0.05	−2.6 ± 0.2	U	it is unknown	−4.7 ± 0.2
Pm	−2.44 ± 0.05	−2.6 ± 0.2	Np	it is unknown	−4.7 ± 0.2
Sm	−1.50 ± 0.01	−1.6 ± 0.2	Pu	−2.59 ± 0.06	−3.5 ± 0.2
Eu	−0.34 ± 0.01	−0.3 ± 0.2	Am	−2.28 ± 0.06	−2.3 ± 0.2
Gd	−2.85 ± 0.07	−3.9 ± 0.2	Cm	−2.78 ± 0.09	−4.4 ± 0.2
Tb	−2.83 ± 0.07	−3.7 ± 0.2	Bk	−2.52 ± 0.05	−2.8 ± 0.2
Dy	−2.56 ± 0.05	−2.6 ± 0.2	Cf	−1.63 ± 0.02	−1.6 ± 0.2
Ho	−2.79 ± 0.06	−2.9 ± 0.2	Es	−1.45 ± 0.01	−1.3 ± 0.2
Er	−2.87 ± 0.08	−3.1 ± 0.2	Fm	−1.18 ± 0.02	−1.1 ± 0.2
Tm	−2.22 ± 0.05	−2.3 ± 0.2	Md	−0.15	0 ± 0.2
Yb	−1.18 ± 0.01	−1.1 ± 0.2	No	+(1.4−1.5)	1.3 ± 0.2

0020-1693/84/$3.00

TABLE II. Ionization Energy Values ΔG°_{ion} and Hydration Energy Values ΔG°_{hydr} (M^{3+}) and ΔG°_{hydr} (M^{2+}) for Lanthanides.

Ln	$-\Delta G^\circ_{ion}$, kJ mol^{-1}	$-\Delta G^\circ_{hydr}$ (M^{3+}), kJ mol^{-1}	$-\Delta G^\circ_{hydr}$ (M^{2+}), kJ mol^{-1}
Ce	1948.8	3192.0	1397.3
Pr	2086.4	3233.4	1308.9
Nd	2132.3	3266.1	1316.9
Pm	2151.6	3297.0	1346.0
Sm	2257.7	3310.4	1344.0
Eu	2404.0	3361.9	1360.9
Gd	1990.5	3379.5	1550.2
Tb	2114.0	3414.2	1463.5
Dy	2199.8	3447.7	1437.2
Ho	2203.7	3469.4	1433.0
Er	2194.1	3489.4	1452.6
Tm	2284.8	3513.4	1451.0
Yb	2416.9	3555.2	1461.1

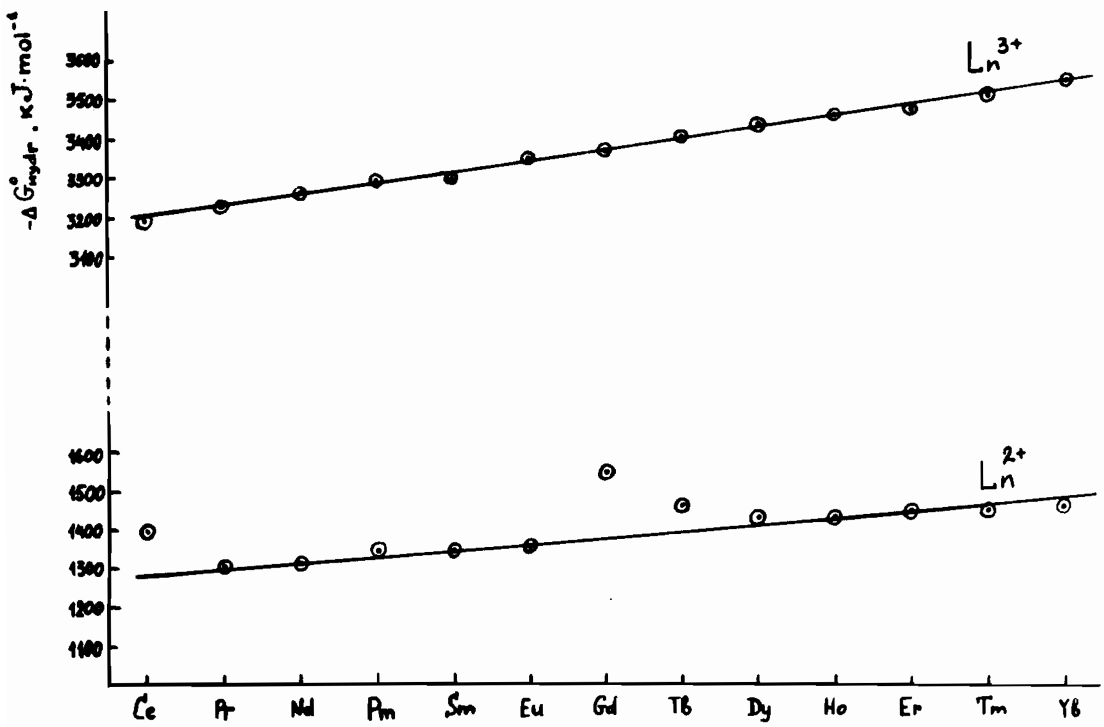

Fig. 1. Hydration Energies for the Divalent and Trivalent Lanthanides.

ions in the trivalent [$\Delta G^\circ_{hydr}(M^{3+})$] and divalent [$\Delta G^\circ_{hydr}(M^{2+})$] states. Accordingly, the standard oxidation potential $E^\circ_{M^{3+}/M^{2+}}$ can be expressed by an equation:

$$F(E^\circ_{M^{3+}/M^{2+}} + 4.43) =$$

$$= \Delta G^\circ_{ion} + \Delta G^\circ_{hydr}(M^{3+}) - \Delta G^\circ_{hydr}(M^{2+}) \qquad (1)$$

where 4.43 is the standard thermodynamic electrode potential of the hydrogen electrode [9]; ΔG°_{ion} is calculated based on the values of the third ionization potential I_3 [10]; $\Delta G^\circ_{hydr}(M^{3+})$ is as described in [11]. All these data on the lanthanides are given in Table II, which also gives the $\Delta G^\circ_{hydr}(M^{2+})$ values calculated using eqn. (1).

As can be seen from Fig. 1, $\Delta G^\circ_{hydr}(M^{2+})$ is changing linearly with an increase in the atomic number of the elements. A similar dependence is observed for $\Delta G^\circ_{hydr}(M^{2+})$ if we disregard the values of Ce^{2+}, Gd^{2+}, and Tb^{2+}. The increased hydration energies for Ce^{2+}, Gd^{2+}, and Tb^{2+}, compared to those calculated using the interpolation and extrapolation method, need special attention.

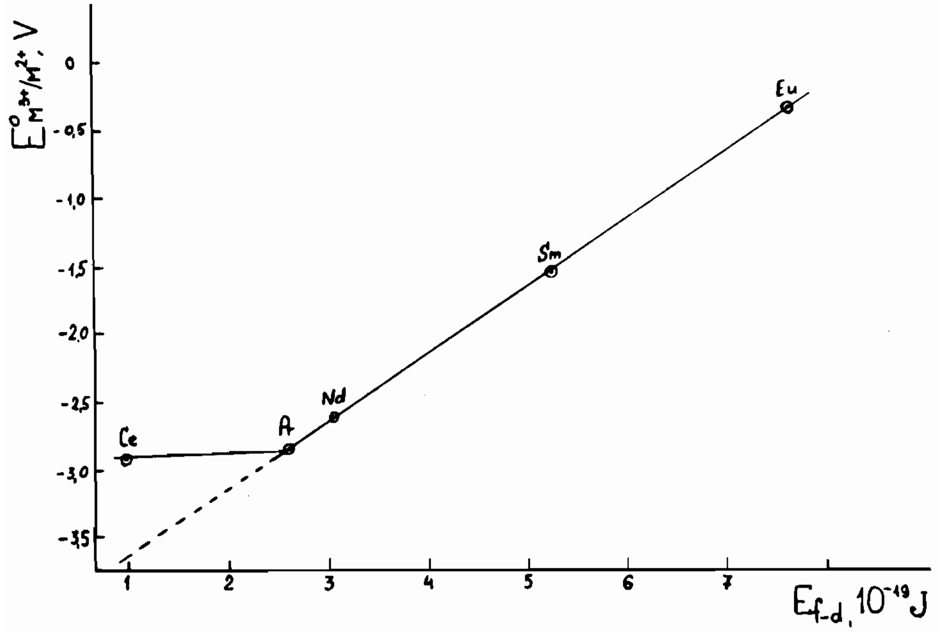

Fig. 2. Dependence of the standard oxidation potentials of the M^{3+}/M^{2+} couples on the f–d excitation energies for the first half of the lanthanides.

TABLE III. Increased Hydration Energies for Ce^{2+}, Gd^{2+}, and Tb^{2+} Compared to the Calculated Data.

Ln^{2+}	Calculated from $\Delta G^\circ_{hydr}(M^{2+}) = f(Z)$, kJ mol^{-1}	Calculated from $E^\circ_{M^{3+}/M^{2+}}\ f(E_{f-d})$, kJ mol^{-1}
Ce^{2+}	104 ± 17	85 ± 11
Gd^{2+}	167 ± 9	173 ± 27
Tb^{2+}	65 ± 9	85 ± 18

Gadolinium in the state of a free double-charged atom is known to have the f^7d electron configuration. Therefore, the $Gd^{3+} + e \rightarrow Gd^{2+}$ reduction is connected with the transition of an electron to a d-orbital. The d-level is known to be subject to substantial splitting in the ligands' field. For instance, the splitting (Δ) of the d-level of Gd^{2+} in the CaF_2 matrix reaches $4.83 \cdot 10^{-19}$ J [12], while the lowering of the d-level depends on the central atom's surrounding, and is approximately one half of Δ. Thus, the energy decrease of the d-level leads to the stabilization of the divalent state which results in a hydration energy increase $\Delta G^\circ_{hydr}(M^{2+})$. As for Ce^{2+} and Tb^{2+}, both these ions do not have d-electrons in a free state. However, their $f^n \rightarrow f^{n-1}d$ excitation energies are not great ($0.66 \cdot 10^{-19}$J for Ce^{2+} and $1.78 \cdot 10^{-19}$ J for Tb^{2+}), and they are lower than the energy decreases of the d-level due to the splitting in the ligands' field. Obviously, the increase in the hydration energies for these ions is just the difference between the energy decreases of the d-level and the $f^n \rightarrow f^{n-1}d$ excitation energies. Therefore, the formation of the $f^{n-1}d$ electron configuration for an ion owing to the splitting of the d-level in the ligands' field is possible in the case when the energy decrease of the d-level exceeds the f–d excitation energy. The increases of the excitation energies of Ce^{2+}, Gd^{2+}, and Tb^{2+} are given in Table III.

The problem of the relationship between $E^\circ_{M^{3+}/M^{2+}}$ and the f–d excitation energies for the lanthanides and actinides [13, 14] has been discussed a number of times. It has been suggested that there is a linear dependence (the coefficient approximately equal to one) between $E^\circ_{M^{3+}/M^{2+}}$ and the f–d excitation energy expressed in eV. So given the experimental data on the standard oxidation potentials $E^\circ_{M^{3+}/M^{2+}}$, it becomes possible to prove this supposition. Actually, a linear dependence between $E^\circ_{M^{3+}/M^{2+}}$ and the f–d excitation energy was found for the elements from praseodimium to europium within the first half of the family (Fig. 2):

$$E^\circ_{M^{3+}/M^{2+}} = (0.80 \pm 0.03)E_{f-d} - (4.12 \pm 0.08) \qquad (2)$$

and from disprosium to ytterbium within the second half of the family (Fig. 3):

$$E^\circ_{M^{3+}/M^{2+}} = (0.84 \pm 0.09)E_{f-d} - (4.64 \pm 0.27) \qquad (3)$$

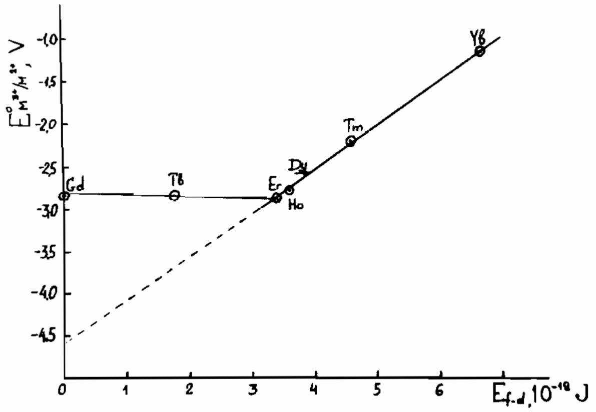

Fig. 3. Dependence of the standard oxidation potentials of the M^{3+}/M^{2+} couples on the f–d excitation energies for the second half of the lanthanides.

where E_{f-d} is the f–d excitation energy expressed in eV.

As it can be noticed, both equations have close parameters. These equations may be compared with eqn. (1) expressed in the following way:

$$F(E^{\circ}_{M^{3+}/M^{2+}} + 4.43) =$$
$$= \Delta G^{\circ}_{f-d} + [\Delta G^{\circ}_{I_d} + \Delta G^{\circ}_{hydr}(M^{3+}) - \Delta G^{\circ}_{hydr}(M^{2+})] \quad (4)$$

where ΔG°_{f-d} is the change of the free energy of the f–d excitation, and $\Delta G^{\circ}_{I_d}$ is the change of the free energy of ionization of Ln^{2+} from the excited $f^{n-1}d$ state.

If the sum of the values in outer brackets is constant within a certain range, then it becomes obvious that equations (2, 3 and 4) are similar. The increase in the oxidation potentials $E^{\circ}_{M^{3+}/M^{2+}}$ of 0.87 V for cerium, of 1.78 V for gadolinium, and of 0.87 V for therbium, compared to the values extrapolated using eqns. (2) and (3) (Figs. 2 and 3), is accounted for, as mentioned above, by an increase in the energy of hydration of divalent ions of these elements, connected with the lowering of the d-level and with the electron's localization at the d-orbital.

As it is seen from Table III, the increase in hydration energies for Ce^{2+}, Gd^{2+} and Tb^{2+}, accounting for the increases in their standard oxidation potentials, is close to the respective values of the increase in the hydration energies calculated from the deviation $\Delta G^{\circ}_{hydr}(M^{2+})$ from the linear dependence on the atomic number of the elements.

Although the oxidation potentials $E^{\circ}_{M^{3+}/M^{2+}}$ are known for all elements from plutonium to nobelium (Table I), the An^{2+} hydration energies are impossible to calculate because the experimental thermodynamic values from eqn. (1) are not available. However, the values of the f–d oxidation energy are known for all An^{2+} [15]. This would enable us to calculate, if not the An^{2+} hydration energy value itself, then its increase in the case of the formation of the $f^{n-1}d$ configuration. As in the case of the lanthanides, the dependence of $E^{\circ}_{M^{3+}/M^{2+}}$ on E_{f-d} is linear (Fig. 4) and can be expressed as:

$$E^{\circ}_{M^{3+}/M^{2+}} = (0.89 \pm 0.11)E_{f-d} - (4.69 \pm 0.42) \quad (5)$$

where the parameters are close to those of eqns. (2) and (3).

Plutonium and curium, however, similarly to Ce, Gd and Tb do not follow the rule. The experimentally-found standard oxidation potentials $E^{\circ}_{Pu^{3+}/Pu^{2+}}$ and $E^{\circ}_{Cm^{3+}/Cm^{2+}}$ turned out to be higher by 0.58 V and 1.12 V than the calculated ones. These differences coincide with the increases in the Pu^{2+} and Cm^{2+} hydration energies by 56.3 kJ mol^{-1} and 108.5 kJ·mol^{-1}. Based on these values of the energy of f–d transitions for Pu^{2+} and Cu^{2+} we calculated the values of energy decreases of the d-level due to the splitting in the ligands' field, being equivalent to $3.6 \cdot 10^{-19}$ J for Pu^{2+} and $3.2 \cdot 10^{-19}$J for Cm^{2+}.

Thus, new data on the divalent states of the lanthanides and actinides were obtained. Certain lanthanides and actinides in the divalent states were shown to have the $f^{n-1}d$ configuration. In this case, they lose their similarity with the alkaline-earth ions and become analogous to the d-elements in lower oxidation states. The elements of the first half of the actinides are characterized by the low energy values of the f–d transitions, which results in the appearance of certain properties normally inherent to the d-elements.

Haissinsky [16] uses a number of arguments in favour of the likeness between the first half of the actinides and the 3d-series elements, including the data on the decrease of ionic radii with an increase in the atomic number of the elements. This decrease is equal to 0.07 Å for the 3d-elements from Ti^{3+} to Mn^{3+}. The same compression is observed for the series from Th^{3+} to Np^{3+} [16]. Referring to Selwood, Haissinsky says that the first half of the 3d-elements shows the same character of change to magnetic susceptibility (with an increase in the atomic number) as that of the first half of the actinides.

As it was noted before [18], it can now be stated that the whole actinide group, and not only the first half, resemble to a certain extent the 3d-elements, as is evident from comparing Fig. 5 and Fig. 6.

The increase in maximum valency from three to seven with an increase in the atomic number is true of the elements of both families. However, both the stability decrease for the higher oxidation states and the stability increase for the lower ones occur in the same direction. The actinides, as well as the 3d-elements, do not reach valency 8 while mendelevium, the second-last element of the actinide

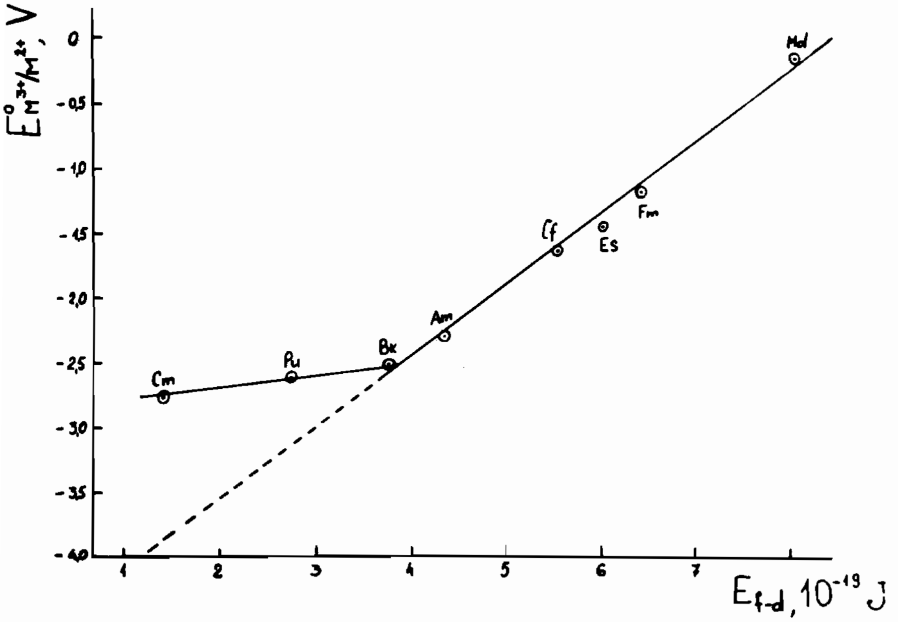

Fig. 4. Dependence of the standard oxidation potentials of the M^{3+}/M^{2+} couples on the f–d excitation energies for the second half of the lanthanides.

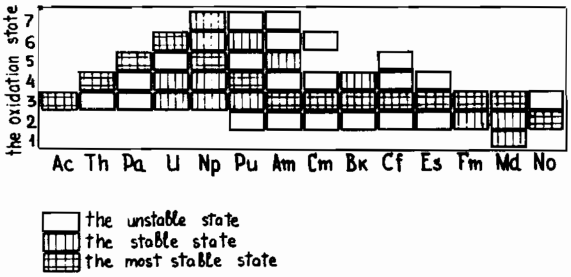

Fig. 5. Oxidation states of the actinides.

group, analogously to copper shows valencies of 3, 2 and 1. This similarity between the 5f- and 3d-elements is accounted for by the same character of the filling of the 5f- and 3d-orbitals by the electrons, as well as a close character of change of electron energies of the 5f- and 3d-orbitals with an increase in the atomic number. A decrease in the energies of electrons at the 3d- and 5f-orbitals for the elements of the second halves of both families lead to the stabilization of the lower oxidation states.

The 3d-elements from iron to zinc (*i.e.* in the direction the 3d-level gets filled) show an increase in the stability of the divalent states. A similar picture is observed for the elements from berkelium to nobelium. The standard oxidation potential $E^{\circ}_{M^{3+}/M^{2+}}$ increases in this direction (Table I). Along with this, as the atomic number of the elements increases, the differentiality of the chemical properties of the elements of both series also increases.

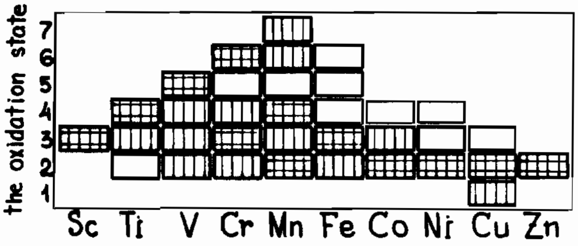

Fig. 6. Oxidation states of the 3d-elements.

Because of larger spacial stretching of the d-orbitals compared to the f-orbitals, the latter are characterized by a smaller overlapping integral which for the second half of the 5f-elements results in a lower ability to form coordination compounds.

The elements of the second half of the actinide family in the trivalent state are known to show a lot of similarity with lanthanides, while in the divalent state they are analogous to alkaline-earth elements. For example, $FmCl_2$ co-crystallizes with $SrCl_2$ owing to isomorphic co-crystallization [19]. Divalent nobelium holds, by its properties, an intermediate position between Ca^{2+} and Sr^{2+} [20, 21]. Divalent fermium does not show a substantial capability to form chloride complexes [22]. The same is true of monovalent mendelevium [23], whose ionic radius lies within the interval of those of Na^+ and K^+ and is equal to 1.2 Å [24], the solubility product of MdCl in ethanolic solutions being close to that of KCl [25].

At the same time, monovalent mendelevium, similarly to Ag^+ but unlike alkaline metal ions, is capable

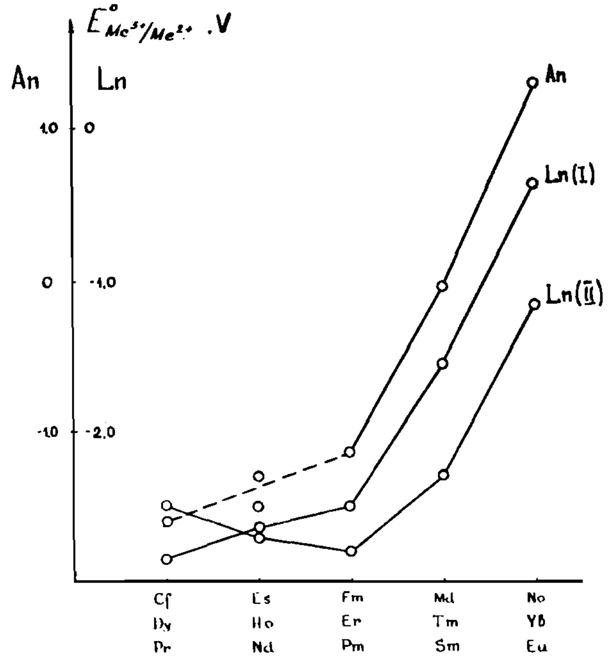

Fig. 7. Standard oxidation potentials $E^\circ_{M^{3+}/M^{2+}}$ of the lanthanides and actinides.

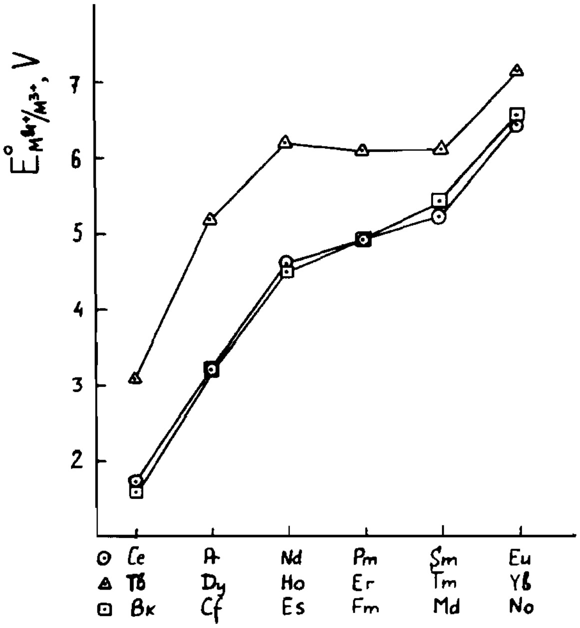

Fig. 8. Standard oxidation potentials $E^\circ_{M^{4+}/M^{3+}}$ of the lanthanides and actinides.

of co-crystallizing with SmF_2 and YbF_2, resulting in the formation of anomalous mixed crystals [23]. The reasons for this phenomenon are not yet clear. It can be viewed both from the point of view of exceptional closeness of the ionic radii of Ag^+ and Md^+, and by assuming a certain chemical analogy between these two elements in the monovalent states.

Besides considering the similarity of the actinides with the 3d-elements, attention should be placed to the problem of similarity between the 4f- and 5f-elements. Postulating his actinide concept, Seaborg viewed the actinide group as a second rare-earth series in which the respective elements of the actinide and lanthanide groups are paired [26, 27]. The idea of pair analogy of the lanthanides and actinides, (*i.e.* the analogy of the elements of both families having equal numbers of f-electrons) is the basic provision of Seaborg's actinide concept. Based on the pair analogy principle, Seaborg has predicted the existence of tetravalent berkelium, which is paired with therbium, and of divalent nobelium, analogous to ytterbium [26, 27].

However, our investigations showed the limited value of the pair analogy idea for the elements of the second halves of lanthanides and actinides [28]. Since Ho^{2+} is very hard to obtain [29], and Er^{2+} had never before been obtained [30] it was wrong to suggest not only the existence of divalent einsteinium and fermium and to neglect the increase in the An^{2+} stability (from Es to Fm) which shows in the increase in the standard oxidation potential $E^\circ_{M^{3+}/M^{2+}}$ (Table I).

The lanthanides from praseodimium to europium are known to have the number of non-pair f-electrons equal to that of undivided pairs at the f-level for the elements from dysprosium to ytterbium and from californium to nobelium. Therefore, owing to the electron-hole symmetry principle, the respective elements from the above mentioned series in the same oxidation states would have terms with the same values of the total orbital moment L. This gives us grounds to compare the above-mentioned series with each other. Figure 7 shows the dependence of the standard oxidation potentials on the atomic number of the elements for the elements of the first half of Ln (from Pr to Eu), the second half of Ln (from Dy to Yb), and the second half of An (from Cf to No). As it is seen from Fig. 7, $E^\circ_{M^{3+}/M^{2+}}$ for the elements of the first half of the lanthanides and the second half of the actinides grow monotonically with an increase in the atomic number of the elements. Despite the fact that $E^\circ_{M^{3+}/M^{2+}}$ for the elements of the respective groups differ approximately by 1V, both curves are amazingly identical. This, however, is not true of the second half of the lanthanides. The oxidation potential decreases from dysprosium to erbium, and then it grows further. Erbium's position is just at the minimum point of the curve line.

This non-monotonical dependence of the change in stability of the 2+ oxidation states for the elements of the second half of the lanthanides cannot be

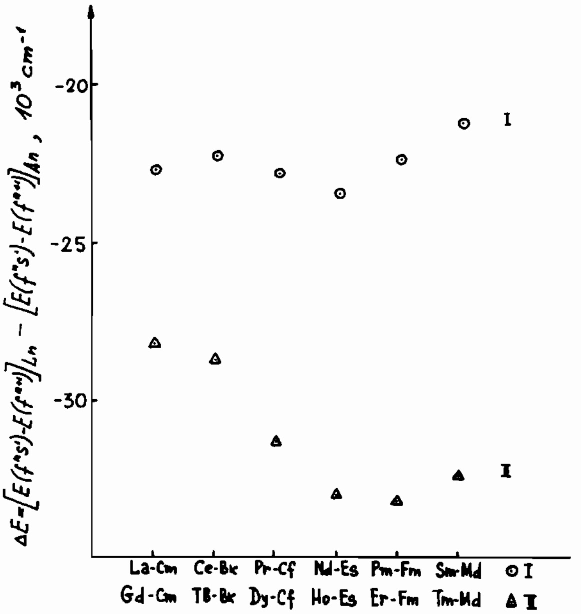

Fig. 9. The s–f excitation energy change for the first and second halves of the lanthanides, compared to that of the second half of the actinides.

explained by a special change in the Ln^{3+} or Ln^{2+} hydration energy since, as is seen from Fig. 1, both these values change similarly with an increase in the atomic number. Thus, the exceptional closeness of the first half of Ln and the second half of An, and a substantial difference of these two groups from the second half of Ln, can be accounted for only by the same character of electron energy change at the 4f- and 5f-orbitals.

It was thus of special attention to find out whether such regularities would show in the cases of losing or acquiring electrons by the f-orbitals. To do this it was necessary to consider the dependence of the stability change for other oxidation states of the lanthanides and actinides on the growth of the atomic number of the elements. Figure 8 shows the dependence of the standard oxidation potentials $E^{\circ}_{M^{4+}/M^{3+}}$ calculated by Nugent on the atomic number for the lanthanides and the second half of actinides.

As it is seen from the figure, the standard oxidation potentials $E^{\circ}_{M^{4+}/M^{3+}}$ for the elements of the first half of Ln and the second half of Ac practically coincide.

The similarity between the first half of the lanthanides and the second half of the actinides shows in the excitation energies of the $f^n s^1 \rightarrow f^{n+1} s^0$ electron transitions which characterize the stability of the monovalent states. Although the calculated values of $f^n s^1 \rightarrow f^{n+1} s^0$ for the actinides cannot claim high accuracy, one can nonetheless witness the similar character (Fig. 9) of the s–f excitation energy change for the elements of the first half of Ln and the second part of An.

Thus, based on the above-mentioned regularities, we can conclude the following. The elements of the first half of the lanthanides and the second half of the actinides are characterized by the same energy change of f-electrons with an increase in the atomic number of the elements, irrespective of the number of electrons at the f-level. This experimental regularity needs theoretical justification. Therefore, when considering the properties of the actinides with regard to the development of the Mendeleev Periodic Law, it is necessary to note that the actinides, as well as the 3d-elements, have similar characters of the electron energy change at the 5f- and 3d-orbitals with an increase in the atomic number of the element. This shows in the close regularities of the change in the valencies of these elements and their magnetic properties with an increase in the atomic number of the elements.

When comparing the 4f- and 5f-elements, a similarity between the first half of the lanthanides and the second half of the actinides was established, resulting in the same character of the change in the standard oxidation potentials and in the excitation energies of f-electrons. In turn, this reflects the same change in the energies of 4f- and 5f-electrons, with an increase in the atomic number of the element groups being considered.

References

1 N. B. Mikheev, *Radiochim. Acta*, N4 (1983).
2 L. J. Nugent, R. D. Baybarz, J. L. Burnett and J. L. Ryan, *J. Phys. Chem.*, *77*, 1528 (1973).
3 N. B. Mikheev, L. N. Auerman, R. A. Dyachkova and I. A. Rumer, *Radiokhimiya*, *25*, 65 (1983).
4 N. B. Mikheev, V. I. Spitsyn, L. N. Auerman, I. A. Rumer and R. A. Dyachkova, *Dokl. AN SSSR*, *261*, 1154 (1981).
5 H. R. Bronstein, *J. Phys. Chem.*, *73*, 1320 (1969).
6 J. C. Sullivan, S. Gordon, W. A. Milac *et al.*, *Inorg. Nucl. Chem. Lett.*, *12*, 599 (1976).
7 N. B. Mikheev, L. N. Auerman and I. A. Rumer, *Z. Neorg. Khim.*, 5 (1983).
8 N. B. Mikheev, L. N. Auerman, V. I. Spitsyn, I. A. Rumer and R. A. Dyachkova, *Izv. AN SSSR, ser. Khim.*, 818 (1982).
9 E. A. Kanevskii, *Dokl. AN SSSR*, *257*, 926 (1981).
10 W. C. Martin, R. Zalubas and L. Hagan, 'Atomic Energy Levels – The Rare-Earth Elements', NSRDS-NBS, 60 (1978).
11 'Lantanoidy', Pod. red. Minkina V. I., Rostov-na-Donu, 28 (1980).
12 K. E. Johnson and I. N. Sandoe, *J. Chem. Soc. (A)*, 1694 (1969).
13 K. Keller, 'Khimiya transuranovukh elementov', M.: Atomizdat., 212 (1976).
14 G. V. Ionova and V. I. Spitsyn, *Radiokhimiya*, *20*, 196 (1978).
15 K. L. Vander Sluis and L. J. Nugent, *J. Opt. Soc. Amer.*, *64*, 687 (1974).

16 M. N. Haissinsky, 'Yadernaya Khimiya i eyo prilozeniya', M.: IL, 238 (1961).
17 P. Selwood, 'Magnetochemistry', N.Y. (1956).
18 N. B. Mikheev, 'Uchenie o periodichnosti. Istoriya i sovremennost', M.: Nauka, 192 (1981).
19 N. B. Mikheev, V. I. Spitsyn, A. N. Kamenskaya, N. A. Konovalova *et al.*, *Radiokhimiya, 20,* 564 (1978).
20 R. J. Silva, W. J. McDowell, O. L. Keller and J. R. Tarrent, *Inorg. Chem., 13,* 2233 (1974).
21 W. J. McDowell, O. L. Keller, P. E. Dittner, J. R. Tarrant and G. N. Case, *J. Inorg. Nucl. Chem., 38,* 1207 (1976).
22 N. B. Mikheev, A. N. Kamenskaya, I. A. Rumer, N. A. Konovalova and S. A. Kulukhin, *Radiokhimiya, 25,* 153 (1983).
23 N. B. Mikheev, V. I. Spitsyn, A. N. Kamenskaya, N. A. Konovalova, Ya. Mikulskii and T. Petryna, *Radiokhimiya, 23,* 736 (1981).
24 N. B. Mikheev, V. I. Spitsyn, A. N. Kamenskaya and S. S. Berdonosov, *Radiochem. Radioanal. Lett., 5,* 257 (1982).
25 N. B. Mikheev, A. N. Kamenskaya, S. S. Berdonosov and S. I. Klimov, *Radiokhimiya, 23,* 793 (1981).
26 G. T. Seaborg, *The transuranium elements, N.N.E.S., 14B,* 261 (1949).
27 G. T. Seaborg, *Nucleonics, 5,* 16 (1949).
28 N. B. Mikheev, V. I. Spitsyn, R. A. Dyachkova and L. N. Auerman, *J. de Physique, 40,* C4-230 (1979).
29 U. Löchner and J. D. Corbett, *Inorg. Chem., 14,* 426 (1974).
30 A. I. Grushko, A. I. Egorov, G. A. Krutov *et al.*, *Radiokhimiya, 20,* 128 (1978).