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The influence of relativistic effects and the crystal field on the properties of actinyl ions

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ABSTRACT. The electronic structure and properties of the most covalent compounds of the actinides, namely the actinyl ions AnO_2^{2+} (An = U, Np, Pu, Am, Cm, Bk, and Cf), have been analysed on the basis of X_α-SW calculations. The regularity of the change in the redox, crystal-chemical, spectral, magnetic, and other properties in a series of compounds containing the actinyl ions has been studied. The strictly regular, regular, or irregular (stepwise) nature of the dependence of different properties on the atomic number of the element is determined by the extent of the participation of the 5*f*- and 6*d*-electrons in chemical bond formation, that is by the crystal field effect and the influence of relativistic spin–orbit coupling.

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I. Introduction

In the last two decades, the regularity of the change in various physicochemical properties in the lanthanide and actinide series with change in the atomic number of the element has been studied, and a large number of models have been developed to explain them.[1] Some of these have survived, while others have been found untenable. The reason for this variety of models is the difficulty of obtaining an adequate description of the compounds of the *f*-elements using purely ionic or purely covalent models.[2] Thus the ionic model describes the properties of the compounds of the trivalent lanthanides effectively, and those of the trivalent actinides less effectively, but provides a poor description of the tetravalent actinides, and cannot be used at all to describe the electronic structure of compounds of An in high oxidation states (An^{V}, An^{VI}, and An^{VII}).

For compounds with a high bond polarity, there is a definite periodicity in the change in their physicochemical properties (P) with change in the atomic number of the element.[3] This is a general feature, and extends to the ionic compounds of both the *f*- and *d*-series and the super-heavy transactinide elements. The properties P of the lanthanides (Ln), actinides (An), or transition *d*-elements (M) with f^q- or d^q-electron configurations change periodically in accordance with the periodic change in the quantum numbers L of the normal terms. Thus in each series there are characteristic double–double effects $d^0-d^5-d^{10}$, $f^0-f^7-f^{14}$, $g^0-g^9-g^{18}$, $h^0-h^{11}-h^{22}$, and in each half of the series pairs of triads $d^0-d^1-d^2$, $d^3-d^4-d^5$, tetrads $f^0-f^1-f^2-f^3$, $f^4-f^5-f^6-f^7$, pentads $g^0-g^1-g^2-g^3-g^4-g^5$, and hexads $h^0-h^1-h^2-h^3-h^4-h^5-h^6$.[3] This periodicity is obviously revealed in the properties of the free atoms. The greater the difference between the atom in a molecule and the free atom, the greater the deviation from periodicity.

The present review deals with the most covalent systems formed by the actinides, namely the so-called actinyl cations AnO_2^{z+} (z = 1, 2), beginning with the uranyl ion UO_2^{2+}, whose stability is comparable to that of the vanadyl ion VO^{2+}. The actinyl ions are present as structural units in many compounds of the pentavalent and hexavalent actinides.

The regularity of the change in the crystal-chemical, redox, thermodynamic, spectral, magnetic, and other properties in the series of actinyl ions is determined by the extent of the participation of the 5*f*- and 6*d*-electrons in chemical bond formation, that is by the deviation from the purely ionic model. The study of these regularities represents a fundamental problem in the physical chemistry of the actinides, namely the problem of the "localisation–delocalisation of the 5*f*–6*d*-electrons", which to some extent can be solved by quantum-chemical calculations of the molecular orbitals (MO) of the ions AnO_2^{2+} or AnO_2^{+}, where An = U, Np, Pu, Am, Cm, Bk, and Cf.

A fundamental feature of the change in energy is the increase in the localisation of the 5*f*-electrons with increase in the atomic number of the actinide Z_{An}, which leads to a decrease in the overlap between the 5*f*-AO of the actinide and the 2*s*, 2*p*-AO of the ligands. Increase in the localisation of the 5*f*-electrons leads to an increase in the energy of excitation of the 5*f*-electrons into electron configurations involving 6*d*- and 7*s*-AO. As a result of these effects, increase in Z_{An} leads to a decrease in the stability of the actinyl and actinoyl ions in an isovalent series. This regularity is observed not only for the cations AnO_2^{2+} and AnO_2^{+} but also for other oxygen-containing molecules and ions, in particular the octahedral oxoanions AnO_6^{z-}.[2]

In the present review we try to analyse various aspects of the problem of the localisation–delocalisation of electrons in the most covalent actinide compounds, namely the actinyl ions, on the basis of the relativistic version of the X_α scattered-wave method, to obtain answers to the following questions:

—which fragments of the energy levels can be most definitely distinguished in AnO_2^{2+} and AnO_2^{+} cations, and to what extent are the electrons localised in these fragments;

—to what extent can these fragments be regarded as components for the series of actinyl and actinoyl ions;

—what changes take place in these fragments under the influence of the equatorial ligands X in AnO_2X_y;

—is it possible to distinguish a predominant electron configuration of an actinide in an ion and to go from it to a structural formula with a definite number of the multiple bonds—single, double, or triple?

The answers to these questions will make it possible to solve the fundamental problem in the chemistry of the actinides: in which cases and for what reasons can we expect a strictly regular, regular, or stepwise change in the properties of the actinyl ions along the series?

II. Experimental studies

1. An—O bond parameters obtained from structural studies and vibrational spectroscopy

A vast amount of experimental material has now been accumulated on compounds containing the actinyl and actinoyl ions of uranium, neptunium, plutonium, and americium.[4–31] The material for the uranyl ion has been reviewed.[32] For the problems formulated above, we shall analyse only the regularity of the change in the physicochemical properties of these ions with increase in Z_{An} observed in experimental studies.

For various reasons, the experimental studies which can be carried out for compounds of the elements from uranium to americium with corresponding compositions make up only a small part of the chemistry of actinyl compounds. Most of the studies relate to the uranyl ion. The properties established experimentally for this ion and its compounds are often extended to the neptunyl ion, and are sometimes extrapolated to the other ions, assuming a linear relationship between P and Z_{An}. As shown below, however, for most properties this relationship is irregular.

We shall end the description of various experimental properties of the actinyl ion series with the formulation of the regularity characterising these properties and with its theoretical interpretation if this follows from the classical MO scheme or with the formulation of the theoretical problem of this interpretation if the change in properties with increase in Z_{An} does not correspond to the semi-empirical classical MO scheme and requires up-to-date calculations.

Because of the exceptional stability of the uranyl ion and the ready availability of uranium, X-ray diffraction studies have been carried out for several hundred compounds of this ion, together with a number of studies for other actinyl ions.[33–40]

All the compounds contain a linear symmetrical or slightly distorted actinyl group. The related compounds of uranium, neptunium, plutonium, and americium are isostructural.[41–46] A common feature of all the compounds is the existence of short An—O distances (R_{An-O}) in contrast to the distances to the other ligands in the equatorial plane (R_{An-X}).

Figures 1 and 2 give the dependence of R_{An-O} on Z_{An} for various compounds. These relationships may be regular [as for $RbAnO_2(NO_3)_3$], strictly regular [as for $NaAnO_2Ac_3$ and $AnO_2(ClO_4)_2$], or irregular (as for $K_3AnO_2F_3$ and $Cs_2AnO_2Cl_4$). $R_{An-O}-Z_{An}$ relationships similar to those in Fig. 1*a* have been called arch-like (Ω-type), and relationships similar to those in Figs. 1*b*, 1*c*, 2*a*, and 2*b* have been called zigzag (*N*-type).[47] It is not always easy to distinguish these two types from the values of the internuclear distances. Thus in Figs. 1*b*, 1*c*, and 2*a* the continuous lines denote relationships of the Ω-type. For these series of compounds, the two types of relationship lie within the experimental error. From an examination of the series of relationships in Figs. 1 and 2 it can be reliably concluded that the internuclear distances R_{An-O} increase with increase in Z_{An} in related compounds of the elements for uranium to americium, and that these relationships are not linear, unlike the dependence of the ionic radii $R_{An^{6+}}$ on Z_{An}.

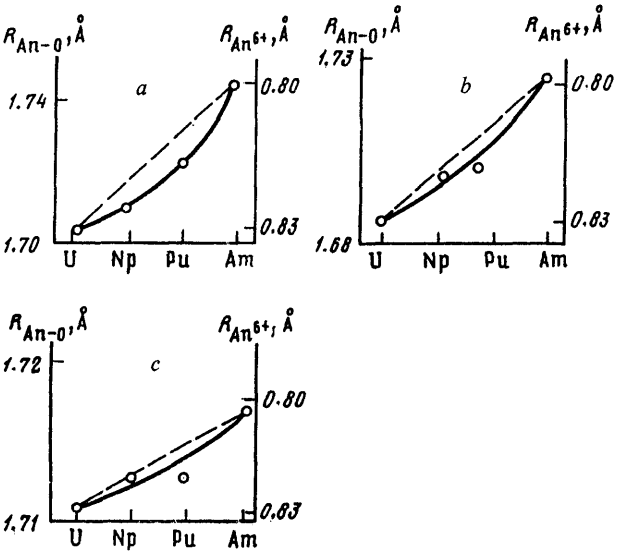


Figure 1. Dependence of the ionic radii of the sextuply-charged ions An^{6+} (broken line) and the internuclear distances R_{An-O} (continuous line) on Z_{An}:[48] *a*, *b*, strictly regular relationships for $NaAnO_2Ac_3$ [32] and $AnO_2(ClO_4)_2$;[35] *c*, regular relationship for $RbAnO_2(NO_3)_3$.[32]

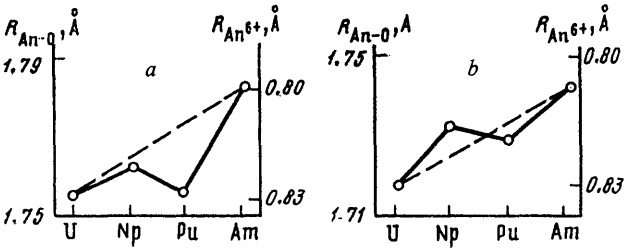


Figure 2. Dependence of the ionic radii of the sextuply-charged ions An^{6+} on Z_{An} (broken line) and the irregular dependence of R_{An-O} on Z_{An} for the compounds $K_3AnO_2F_3$ (*a*) [15] and $CsAnO_2Cl_4$ (*b*).[32]

Both types of relationship (Ω- and *N*-types) can be observed in other properties of the actinyl ions, and a qualitative explanation is not simple. Thus the ionic radii of the sextuply-charged actinide ions are 0.83, 0.82, 0.81, and 0.80 Å for uranium, neptunium, plutonium, and americium respectively.[48] If it is assumed that the ionic radius of the O^{2-} ion is 1.36 Å, the values of R_{An-O} in the actinyl ions of uranium, neptunium, plutonium, and americium should be 2.19, 2.18, 2.17, and 2.16 Å respectively. The experimental values of R_{An-O}, however, not only are 0.5 Å shorter but also change in the opposite order with increase in Z_{An}.

Thus an important problem in structural theory is to establish a direct relationship between the electronic structure of the actinyl ions and the non-additive, regular, or irregular increase in the internuclear distances R_{An-O}. The question of whether the *N*-type of relationship observed for the internuclear distances R_{An-O} is determined by the electronic structure of the free actinyl ions or by the influence of the equatorial ligands still remains open.

The changes in R_{An-O} are to some extent reflected in the values of the force constants of these bonds K_{An-O} in hexavalent actinyl compounds. The change in K_{An-O} for related compounds of uranium, neptunium, and americium shows a number of characteristic features.

1. The force constants of the An–O bonds decrease on going from the uranyl to the americyl ion. Our estimates of K_{An-O} for the curyl ion indicate a further decrease in the strength of the actinide–oxygen chemical bond. These results correspond to increasing localisation of the 5*f* electrons with increase in Z_{An} and increase in the number of antibonding electrons.

2. The change in K_{An-O} with change in Z_{An} is non-additive, and two types of deviation from additivity are observed: positive for $NaAnO_2Ac_3$ (70.8, 69.7, 67.5, 63.4 μdyn nm^{-1}) and $AnO_2(ClO_4)_2$ (77.5, 78.1, 77.1, 73.5 μdyn nm^{-1}) and negative for $Cs_2AnO_2Cl_4$ (68.0, 65.1, 63.6, 62.7 μdyn nm^{-1}).

3. Finally, it is possible to distinguish two types of $K_{An-O}-Z_{An}$ relationships, namely Ω- and *N*-types. Naturally, the separation of the curves into Ω- and *N*-types involves certain assumptions, as in the case of the internuclear distances.

For the perchlorate complexes, the force constant increases on going from the uranyl to the neptunyl ion. This is possibly due to errors in the measurement of the wavenumber of the antisymmetric stretches ν_{as} for U^{6+} or Np^{6+}. Morss[49] gives the same value ν_{as} = 935 cm^{-1} for the two ions, taken from an early paper.[50]

For the fluoride complexes of plutonium and neptunium, $K_{Pu-O} > K_{Np-O}$. A decrease in ν_{as} and K_{An-O} with increase in Z_{An} appears more logical if it is assumed that the influence of the equatorial ligands on the electronic structure of the cations is the same for all cations.

There are fewer published X-ray diffraction studies for compounds containing pentavalent actinoyl ions than for their hexavalent analogues.[51–56]

Studies of compounds containing AnO_2^{2+} and AnO_2^{+} ions reveal many common features in the stereochemistry of these complexes, namely in the values of the coordination numbers (CN) and the types of coordination polyhedra. Naturally, all the interatomic distances R_{An-O} in the actinoyl compounds are greater than those in the corresponding actinyl analogues. On the average, the difference in the bond lengths R_{An-O}, where An = Np and U, is 0.012 ± 0.006 nm.

A complete set of values of K_{An-O} and R_{An-O} for all the actinoyl ions is not available. The use of some published data[49,50] for $NpO_2(ClO_4)_2$ and $AmO_2(ClO_4)_2$ gave the following values of K_{An-O} for the AnO_2ClO_4 series (in μdyn nm^{-1}): 53.1, 56.5, 58.6, and 57.7 for An = U, Np, Pu, and Am respectively, and the use of other data[35] gave the values 50.1, 52.5, 52.9, and 50.7 μdyn nm^{-1} respectively. The $K_{An-O}-Z_{An}$ relationships observed are of the same Ω-type observed for the actinyl compounds with the same perchlorate anions.

Thus each of the above characteristics of the change in K_{An-O} with increase in Z_{An} represents a problem for quantum-chemical interpretation.

2. Optical spectra

The interpretation of the electronic–vibrational spectra[57–62] and the optical spectra by the method of molecular orbitals (MMO)[63–69] has led to important conclusions about the nature of the chemical bond in the actinyl series. In compounds containing "yl" groups, two types of electron transition have been detected in the visible range: uranyl-like charge-transfer transitions E_{CT} and *f*–*f* transitions. The first correspond to the excitation of an electron from a higher bonding MO of predominantly 5*f*-character. For the actinyl anions AnO_2^{2+}, the values of E_{CT} for An = U, Np, Pu, and Am are respectively 20679 ± 472, 13358 ± 338, 15396, and 10086 cm^{-1} [70–73] (Fig. 3).

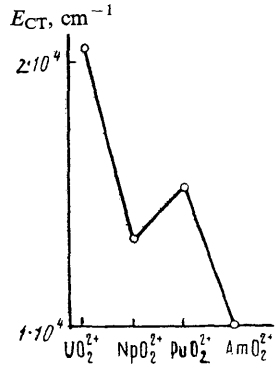


Figure 3. Dependence of the energy of the uranyl-like charge-transfer transition (E_{CT}) in actinyl ions on the atomic number of the acitnide.

Table 1. Energies of the *f*–*f* electron transitions for AnO_2^{2+} (cm^{-1}).[69]

Transition	NpO_2^{2+}	PuO_2^{2+}	AmO_2^{2+}
$\varphi_{5u}-\delta_{3u}$	-	-	-
$\varphi_{5u}-\varphi_{7u}$	6750	-	-
$\varphi_{5u}-\delta_{5u}$	8180	12024	13630
$\varphi_{5u}-3\pi_{1u}$	18180	19193	19300
$\varphi_{5u}-3\pi_{3u}$	21100	24040	-
$\delta_{3u}-\delta_{5u}, \varphi_{7u}$	-	10186	11710
$\delta_{3u}-3\pi_{1u}$	-	16060	16190
$\delta_{3u}-3\pi_{3u}$	-	21320	21420

For NpO_2^{2+}, a series of absorption bands has been detected with energies 13918, 16072, 16092, 7967, and 1951 cm^{-1} [70] or 13239, 15402, 15678, 16795, 19371 cm^{-1}.[71] For PuO_2^{2+} the values of E_{CT} are 15280, 15498, and 15658 cm^{-1}.[72]

In the sequence of E_{CT} values for the actinyl ions, a red shift is observed. The same shift should obviously be observed in the values of E_{CT} for the actinoyl ions.

The energies of the $f-f$ transitions are given in Table 1.[69] The energies of transitions of the same kind tend to increase with increase in Z_{An}.

There are few published experimental data on the values of the energies of the $f-f$ transitions for compounds containing actinoyl ions. For example, for the absorption wavenumbers of $Cs_3NpO_2Cl_4$ the ranges 6035–11111, 16437–22309, and 12810–15973 cm^{-1} have been given.[71]

The transitions of greatest interest for analysing the chemical bonding in actinyl compounds are the uranyl-like transitions, whose energies change irregularly along the series UO_2^{2+}, NpO_2^{2+}, PuO_2^{2+}, AmO_2^{2+}, giving an N-type relationship.

3. Redox potentials

The formal potentials E^0 in perchlorate solutions have been determined experimentally for the AnO_2^{2+}/AnO_2^{+} couples; the values obtained are 0.089 ± 0.002, 1.160 ± 0.005, 0.940 ± 0.004, and 1.624 ± 0.009 for An = U, Np, Pu, and Am respectively.[74] Fig. 4 shows that the dependence of E^0 on Z_{An} is irregular (N-type). Comparison of Figs. 3 and 4 shows an analogy in the changes in E_{CT} and E^0 with change in Z_{An}, leading to a linear relationship between E_{CT} and E^0 (Fig. 5).

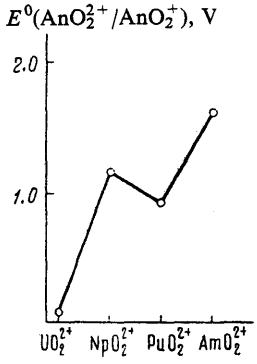


Figure 4. Dependence of the redox potentials (E^0) of AnO_2^{2+}/AnO_2^{+} couples on Z_{An}.

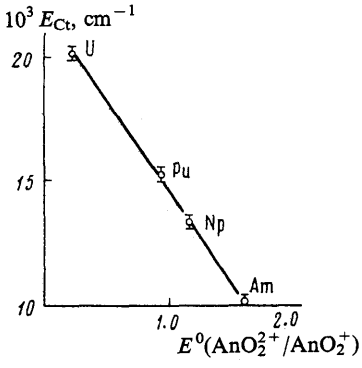


Figure 5. Linear relationship between the calculated energy of the uranyl-like transitions (E_{CT}) of the actinyl ions[123] and the measured redox potentials.[74]

The irregular change in the redox potentials may be due either to the specific features of the electronic structure of the actinyl ions themselves or to the influence of the equatorial ligands; this is again a problem for theoretical study. In any case, it is impossible to avoid semi-empirical MO schemes for an explanation of the irregular changes in the redox properties. From general qualitative considerations it is obvious that the redox potentials increase towards the end of the first half of the series, in particular from the uranyl to the americyl ion. The extremal change in E^0 for the PuO_2^{2+}/PuO_2^{+} couple, however, does not fit into the usual qualitative interpretation.[75–77]

4. Thermodynamic properties

The free energies and enthalpies of the actinyl and actinoyl ions have been discussed.[33,34,49] Fig. 6 shows the dependence of the standard enthalpies of formation of the actinyl (a) and actinoyl (b) ions on the atomic number of the actinide. In both cases the relationship is strictly regular. We noted above that the redox potentials $E^0(AnO_2^{2+}/AnO_2^{+})$ of the chemical reactions

$$(AnO_2^{2+})_{aq} + e \rightarrow (AnO_2^{+})_{aq}\,, \qquad (1)$$

for the same sequence of actinyl ions change irregularly. The change in free energy for reaction (1) can be written as

$$\Delta G_0^0 = FE^0(AnO_2^{2+}/AnO_2^{+}), \qquad (2)$$

where F is the Faraday constant, or

$$\Delta G_0^0 = \Delta G_0^0(AnO_2^{2+})_{aq} - \Delta G_0^0(AnO_2^{+})_{aq}\,. \qquad (3)$$

Comparison of Eqns. (2) and (3) shows that with a regular change in both terms in Eqn. (3), their difference can be represented by an irregular relationship.

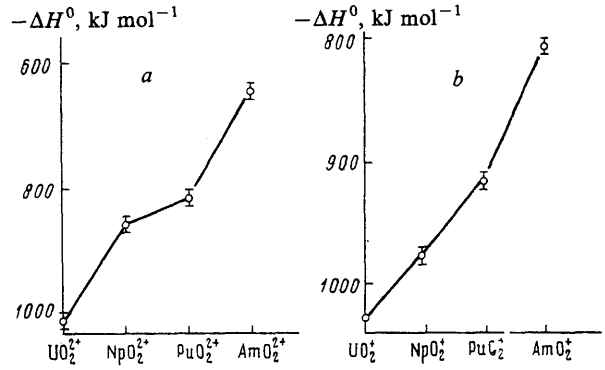


Figure 6. Change in the standard enthalpy of formation of actinyl (a) and actinoyl (b) ions.[30]

Fig. 6b shows that the dependence of $\Delta H^0(AnO_2^{+})$ on Z_{An} is almost linear, whereas the dependence of $E^0(AnO_2^{2+}/AnO_2^{+})$ and $\Delta H^0(AnO_2^{2+})$ on Z_{An} is of the N-type. This important feature,

characteristic of actinyl ions, will be examined below in relation to the electronic structures of these ions.

Finally, the molar polarisability R_M [47] and the refractive index n_d [78] show an identical tendency to undergo an irregular change of the *N*-type with change in Z_{an}. It can be shown that the enthalpy of formation of the actinyl ions and the molar polarisability and refractive index depend on the same parameters related to the electronic structure of the actinyl ions. One of the most important problems in the theory of the structure of the actinyl ions is to find these parameters and identify the fine difference in the electronic structures of the ions which gives an irregular relationship of the *N*-type when revealed in some properties, and a regular relationship when it is not revealed.

5. Extraction of the actinyl ions

There are now extensive published data on the extraction of lanthanides and actinides by various extracting agents.[79–85] Two approaches to the theoretical interpretation of the results may be noted.

A correlation has been noted[80–83] between the change in lg *D*, where *D* is the extraction coefficient for different extracting agents, and the orbital quantum numbers *L* for the normal terms of the *f*-ions. At the same time, a *J*-model has been used,[79] that is it has been shown that in the extraction of tervalent lanthanides by tributyl phosphate (TBP), the change in lg *D* follows the values of the quantum numbers *J* of the normal terms of the free ions, as in the case of the magnetic properties of the lanthanides.

The change in the free energy of extraction

$$\Delta G_e^0 = -RT \lg D ,$$

decreases both with increase in the quantum number *L* and with increase in the quantum number *J*. In the ionic approximation for the series of actinyl ions $U^{6+}(^1S_0)$, $Np^{6+}(^2F_{5/2})$, $Pu^{6+}(^3H_4)$, and $Am^{6+}(^4I_{9/2})$ being considered, the change in the free energy of extraction ΔG_e^0 should decrease regularly from the uranyl ion to the americyl ion if it is assumed that $\Delta G \simeq -L$ or $\Delta G \simeq -J$. In the extraction of the actinyl ions by solutions containing TBP and mineral acids (HNO_3, $HClO_4$, or HCl), the value of ΔG_e^0 when nitric and perchloric acids are added to TBP increases on going from the uranyl to the plutonyl ion, but when hydrochloric acid is added, the value decreases on going from the uranyl to the neptunyl ion and increases on going from the neptunyl to the plutonyl ion.[84] The main conclusion from these experimental data is that the thermodynamic parameters of the extraction of the actinyl ions reflect changes taking place in the electronic structures of these ions on complex formation in the aqueous phase.

6. Complex formation by actinyl ions

Comparison of the values of lg *K* (*K* represents the formation constants of the complexes AnO_2SO_4, $AnO_2(SO_4)_2^{2-}$, $AnO_2(CO_3)_2^{2-}$, $AnO_2(CO_3)_3^{4-}$, AnO_2H^+, $(AnO_2)_2(OH)_2^{2+}$, and $(AnO_2)_3(OH)_5^+$ (in aqueous solution at 25 °C[85–89]) shows two types of lg $K-Z_{An}$ relationships (curves *1*–*7* in Fig. 7).

The first type of relationship is characterised by extremal values of lg *K* for the neptunyl ion (curves *2*–*5* in Fig. 7), and the second corresponds to a regular increase (curve *1* in Fig. 7) or decrease (curves *6* and *7* in Fig. 7) in the values of lg *K*. The change in lg *D* for the actinyl ions, where *D* is the extraction coefficient, shows a regular decrease with increase in Z_{An} for 0.6 M HNO_3 + TBP solution (curve *8* in Fig. 7), and an extremal value for the neptunyl ion in the case of 2 M HCl + TBP solution (curve *9* in Fig. 7).

Thus the change in the thermodynamic parameters in extraction reflects their change on complex formation, that is complex formation is the most important stage determining the thermodynamics of the extraction process. It follows from published data[84] that the entropy term is responsible for the change in ΔG^0 on formation of the di- and tricarbonate complexes of the actinyl ions, and that the enthalpy term is responsible in the case of the mono- and disulphate complexes. In all cases examined except $AnO_2(CO_3)_3^{4-}$, the enthalpy and entropy terms show opposite trends in the change with increase in Z_{An}.

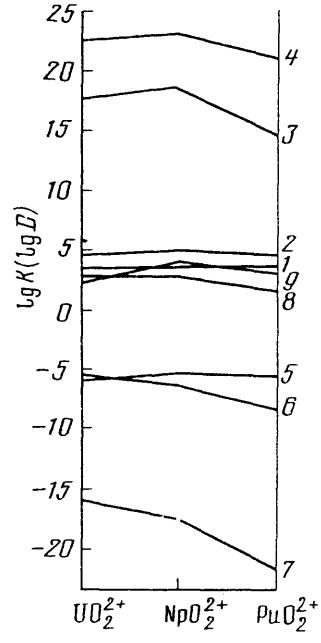


Figure 7. Change in lg *K* (*K* is the equilibrium constant of the reaction $AnO_2^{2+} + X \rightarrow AnO_2X$ in aqueous solution at 25 °C) and ln *D* (curves *8* and *9*) for actinyl ions extracted in 0.6 M aqueous solution by HNO_3 + TBP (*8*) and HCl + TBP (*9*) 25 °C:[84] *1*, AnO_2SO_4;[86] *2*, $AnO_2(SO_4)_2^{2-}$;[86] *3*, $AnO_2.(CO_3)_2^{2-}$;[87] *4*, $AnO_2(CO_3)_3^{4-}$;[88] *5*, AnO_2H^+;[87] *6*, $AnO_2(OH)_2^{2+}$;[89] *7*, $(AnO_2)_3(OH)_5^+$.[89]

The dependence of these thermodynamic parameters on Z_{an} for the extraction of AnO_2^{2+} from HNO_3 + TBP and HCl + TBP solutions shows[84] that in the extraction by nitric acid the trends in the changes in the free energy and the entropy term are the same, whereas in the extraction by hydrochloric acid the trends in the changes in the free energy and the enthalpy term are the same. The experimental data show that in almost all cases examined, the neptunyl ion shows an extremal (or irregular) change in the thermodynamic functions on complex formation or extraction.

In the extraction of the actinyl ions by HNO_3 or $HClO_4$ solution[84] and on formation of the complexes $AnO_2(CO_3)_2^{2-}$ and $AnO_2(CO_3)_3^{4-}$, the free energy and the entropy term change in the same sense with increase in Z_{An}. In the extraction by HCl solution

and on formation of the sulphate complexes AnO_2SO_4 and $AnO_2(SO_4)_2^{2-}$, the free energy and the entropy term change in the opposite sense.[90–95]

III. Electronic structure of the actinyl ions

1. Theoretical studies of actinyl and actinoyl ions

The first model of the molecular orbitals of the uranyl ion, proposed by Eisenstein and Pryce[96] in 1955, was designed to explain the magnetic properties of uranyl compounds. Subsequent studies[65,66,97] were aimed at interpreting the optical spectra of the uranyl ion, and the discussion was based entirely on the MO method. The very first applications of the MO method to the description of the structure of the uranyl ion gave important results. The MO of the uranyl ion were classified on the basis of general symmetry properties; calculations of the overlap integrals made it possible to obtain a measure of the interaction of the atomic orbitals of uranium and oxygen and to determine the principal features of the sequence of the bonding MO of the uranyl ion. The first attempts were made to interpret the magnetic properties and absorption spectra of uranyl compounds.[98–101]

The first quantitative calculations of the molecular orbitals of the uranyl ion were carried out using the theory of the SCF-X_α-method, which makes it possible to obtain a good description of many-electron systems, in particular the complexes of *f*-elements.[102] Calculations carried out up to the present have been restricted mainly to the study of the electronic structure of the uranyl ion by different methods,[103–113] some of which cannot give a clear quantitative picture of the electron density distribution and the structure of the energy levels.[114,115] There is no doubt that it is important to take account of relativistic effects in systems containing heavy atoms.[116–118] There are no published studies, however, of the electronic structure of plutonium and the transplutonium elements, which would make it possible to follow the changes in electronic structure in the actinyl ion series. Until recently there were no published data on the quantum-chemical study of the actinoyl ions, that is there were no published systematic studies of the electronic structure of the series of ions AnO_2^{2+} and AnO_2^{+}. This problem has been examined and reviewed[119–123] using a relativistic version of the X_α-SW method.

2. Calculation procedure

The completely relativistic X_α-SW method is based on the solution of the Dirac equation by the multiple-scattering method.[124]

All the studies have been carried out in the quasi-relativistic (QR) approximation of the SCF-X_α method.[125–133] The essential feature of the QR approximation is the change, for the radial wavefunctions, from the four-component Dirac spinors to two-component spinors with simultaneous exclusion of spin–orbit coupling and neglect of contributions from small components in the construction of the self-consistent central potential and the total electron density. After obtaining self-consistent QR orbitals, spin–orbit coupling was taken into account using perturbation theory and a basis set of QR orbitals, determined with allowance for such relativistic effects as the dependence of mass on velocity and Darwin interaction. The differential equation for the radial function G_{nl} of a large component has the form:

$$[H_{NR} + H_m + BH_D]\, G_{nl} = E_{nl} G_{nl}\,.$$

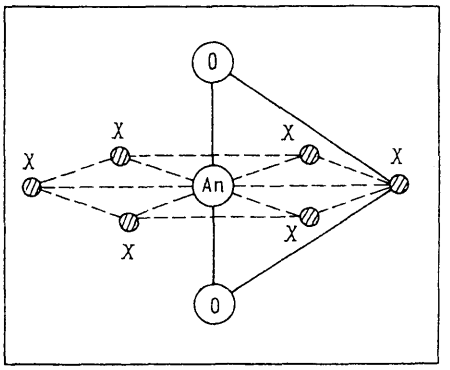


Figure 8. Model of the cluster of an actinyl ion with six ligands X in the equatorial plane of the O–An–O group.

Here, H_{NR} is the standard non-relativistic operator, used to describe the central field (with an exchange $X_\alpha l$-potential), H_m the standard operator for the dependence of the mass of the electron on velocity, and H_D the Darwin operator.[134] The operator B has the form

$$B = \{1 + (\alpha^2/4)[E_{nl} - V(r)]\}^{-1},$$

where $\alpha = 1/137$, and $V(r)$ is the one-electron potential of the central field. The effects of spin–orbit coupling on the molecular orbitals are calculated using perturbation theory in a basis set of self-consistent quasi-relativistic orbitals: $H'_{so} = BH_{so}$, where H_{so} is the standard operator of spin–orbit coupling from Pauli theory.[135–148] As basis orbitals it is possible to use either individual orbitals with a given characteristic value (RX_α-*SO* calculation) or groups of orbitals with similar characteristic values (RX_α-*SO'* calculation, higher orders of perturbation theory).[148–156]

3. Results of the calculations

Model calculations have been carried out[116–120] for the ions AnO_2^{2+} and AnO_2^{+} (An = U, Np, Pu, Am) with interatomic distances R_{An-O} decreasing in accordance with the actinide contraction: 1.73, 1.72, 1.71, 1.70 Å in AnO_2^{2+} and 1.76, 1.75, 1.74, 1.73 Å in AnO_2^{+} for U, Np, Pu, Am respectively. In the works cited, however, no account was taken of the fact that the equatorial ligands X in compounds AnO_2X_y (Fig. 8) have a significant influence on the interatomic distances R_{An-O}, leading, firstly, to their increase with increase in the atomic number of the actinide element, and not to their decrease, as predicted by the effect of actinide contraction and, secondly, to an irregular dependence of R_{An-O} on Z_{An}. We carried out analogous calculations for the actinyl ions in the series of isostructural compounds $NaAnO_2Ac_3$ (a), $Cs_2AnO_2Cl_4$ (b), $RbAnO_2(NO_3)_3$ (c), and $AnO_2(ClO_4)_2$ (d) with different types of dependence of R_{An-O} on Z_{An}. The values of R_{An-O} for all series of compounds with An = U, Np, Pu, and Am respectively (in Å) are given below:

Series	U	Np	Pu	Am
(a)	1.704	1.709	1.721	1.743
(b)	1.1718	1.733	1.731	1.747
(c)	1.683	1.692	1.692	1.712
(d)	1.673	1.670	1.675	1.695

Fig. 9 gives the energy level diagrams for the sequence of doubly-charged AnO_2^{2+} cations, obtained in RX_α-SO′ approximations. The sequence of energy levels remains practically unchanged to the end of the series for different forms of dependence of R_{An-O} on Z_{An}.

The lowest-lying MO ($1\sigma_g - 2\sigma_u$) are formed by the strong covalent mixing of the 6*p*-AO of the actinide and the 2*s*-AO of oxygen, and are inner valence molecular orbitals (IVMO). Above them there is a group of levels formed mainly by the 6*d*- and 5*f*-AO

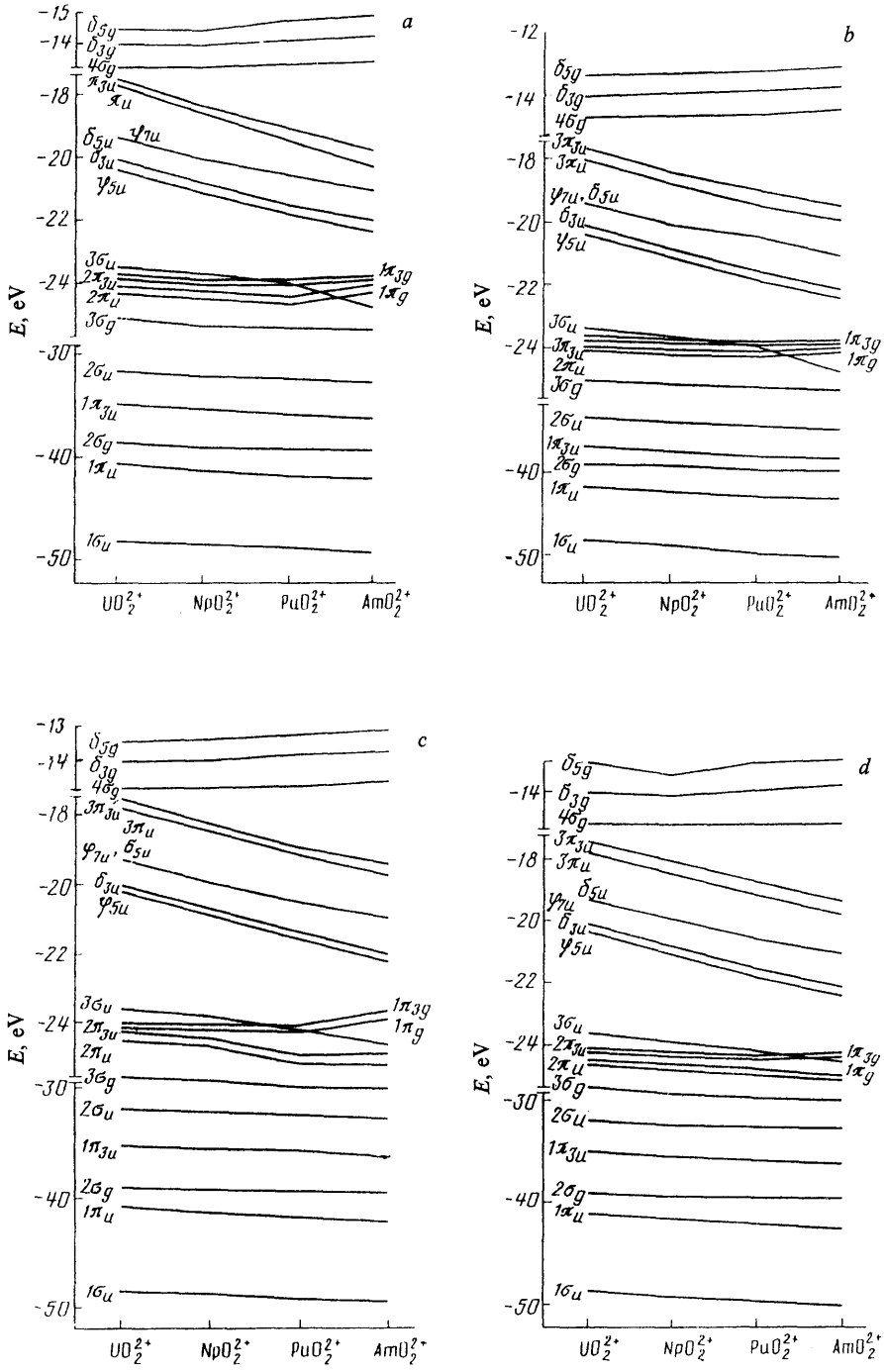


Figure 9. Energies of the MO in actinyl ions calculated by the RX_α-SO′ method: *a*, $NaAnO_2Ac_3$; *b*, $Cs_2AnO_2Cl_4$; *c*, $RbAnO_2 \cdot (NO_3)_3$; *d*, $AnO_2(ClO_4)_2$.

of the actinide and the 2*p*-AO of oxygen, the so-called outer valence MO (OVMO). Even higher, separated by an energy gap (ΔE), are the non-bonding and antibonding levels of 5*f*-character. In the RX_α-SO′ approximation the orbitals φ_{7u} and δ_{5u} are accidentally degenerate. This leads to a qualitative similarity in the electronic structures of the actinyl ions, making it possible to distribute their energy levels of similar composition in groups. In this sense it is possible in the actinyl ions to distinguish the following fragments corresponding to the maximum bonding between various AO: 6*s*(An) + 2*s*(O); 6*p*(An) + 2*s*, 2*p*(O); 5*f*, 6*d*(An) + 2*p*(O); 5*f*(An); and 6*d*(An).

The highest bonding MO (HBMO) for UO_2^{2+} and NpO_2^{2+} is the $3\sigma_u$-MO, but from PuO_2^{2+} and beyond, the π_g-orbital becomes the HBMO. Fig. 9 shows that on going to the heavier actinides, the energies of the non-bonding and anti-bonding MO (of 5*f*-character) gradually decrease, whereas those of the highest bonding MO remain almost unchanged. The greater lowering of the levels of 5*f*-character takes place as a consequence of the gradual increase in the number of electrons localised in them, and also as a consequence of the fact that the energies of the 5*f*-AO decrease with increase in the atomic number of the actinide. The energies of the bonding MO, where the main contribution is made by the AO of oxygen, remain practically unchanged. The magnitude of ΔE decreases along the series from 3.2 eV for UO_2^{2+} to 1.5 eV for AmO_2^{2+}.

Analysis of the electronic structure of the actinyl ions clearly shows the existence of common characteristic groups of levels both in the system of bonding levels and in the system of antibonding levels, corresponding to the interactions 2*s*−6*p*, 2*s*, 2*p*−6*p*, 2*p*−6*d*,5*f* between the valence 2*s*,2*p*-AO of the ligands and the 6*p*, 6*d*, and 5*f*-AO of the actinide atoms from uranium to californium.[122]

Separation of the energy levels into fragments is observed for all the oxygen-containing compounds of the actinides. Comparison of the analogous groups of levels in the isovalent anions and cations, for example in UO_6^{6-} and UO_2^{2+}, NpO_6^{6-} and NpO_2^{2+}, etc., shows, however, that the electrons are more localised in the anions than in the cations. This means that in the anions, in the fragments mainly responsible for their properties, the 2*p*−6*d*,5*f*-electrons are localised to a greater extent in the 2*p*-AO of the oxygen atoms in the bonding levels, and in the 5*f*-AO in the antibonding levels. In the anions, the electronic structure of the fragments is closer to that of the free atoms, that is the bonding levels (2*p*−6*d*,5*f*) approach 2*p*(O), and the antibonding levels (6*d*,5*f*−2*p*) approach 6*d* + 5*f*(An). It can be stated definitely that the series of actinyl ions is described by a set of transferable fragments in such a way that with each of them it is possible to associate a certain energy increment. The cations differ mainly in the electron distributions in the fragments.

In the inner valence MO the most probable distribution of electron density corresponds to its displacement into the 6*s*- and 6*p*-AO of the actinide. In the outer valence MO, the electron density distribution corresponds to covalent bonding.

Finally, in the series of non-bonding and antibonding levels the displacement of electron density corresponds to the direction An←2*p*(O), that is for an anion taken separately the completely "classical" electron density distribution is obtained, and it is preserved in all the actinyl ions. On going from one cation to another, a qualitative modification of the fragments takes place, involving the greater localisation of the 5*f*-electrons with increase in Z_{An} in AnO_2^{2+}, less extensive participation of the 6*d*- and 7*s*-electrons in chemical bond formation, gradual localisation of the core 6*s*- and 6*p*-electrons, and a lowering of the corresponding energy levels.

All this decreases the strength of the An−O bond in the actinyl ions with increase in Z_{An}, and gives a general picture of their qualitative change. This qualitative picture is insufficient, however, for the interpretation of the chemical properties.

Thus the gradual localisation of electrons in the fragments of the actinyl ions with increase in the atomic number of the actinide should have corresponded to a gradual and regular change in their properties.[157–164] The properties of the actinyl ions (from uranyl to americyl), however, generally change in irregular fashion.[1] This means that it is necessary to take account of the difference in the structures of the fragments;[165–170] the transferability of the fragments gives only the zeroth approximation to the qualitative picture.

4. Interpretation of the experimental properties of the actinyl and actinoyl ions, based on the results of SCF-X_α-SW calculations

We shall begin the discussion of the experimental properties with the most important chemical property—the redox potential of the AnO_2^{2+}/AnO_2^{+} couple. The available experimental data give a relationship of the *N*-type for the redox potentials in the series from the uranyl to the americyl ion. To explain this dependence of E^0 on Z_{An}, we can first examine the ionic model, that is the ionisation of the free ions in the gas phase or in solution

$$An^{z+}(f^q) \rightarrow An^{z+1}(f^{q-1}) + e. \qquad (4)$$

The oxidation potential of this reaction under equilibrium conditions is written as:

$$E^0 = \frac{0.05916}{n} \ln K_p, \qquad (5)$$

where K_p is the chemical ionisation equilibrium constant. The free energy of this reaction ΔG^0 and K_p are related by the familiar expression

$$\Delta G^0 = -RT \ln K_p. \qquad (6)$$

At the same time, for standard conditions:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0. \qquad (7)$$

Thus each of the quantities ΔG^0, E^0, and $\ln K_p$ can be calculated in terms of the others if they are related to reaction in the same phase, that is solution or gas. Thus, for the chemical equilibrium constant in the gas phase we readily obtain

$$K_p(T) = \frac{g(f^q)}{2g(f^{q-1})} \left(\frac{2\pi}{m}\right)^{3/2} \frac{h^2}{T^{5/2}} \exp(\Delta E/kT), \qquad (8)$$

where $g(f^q)$ and $g(f^{q-1})$ are the statistical weights of the normal states of the ions $An^{z+}(f^q)$ and $An^{z+1}(f^{q-1})$, *m* the mass of the ion, *T* the temperature, and ΔE the energy difference between the normal terms of the ions with the f^q- and f^{q-1}-electron configurations.

It can readily be shown that at *T* = constant for all the ions, completely neglecting covalent effects, the change in K_p along the series depends on the ratio $g(f^q)/g(f^{q-1})$, and the change in the free energy of the redox reaction (4) being considered, in accordance with Eqn. (6), depends on the logarithm of this ratio, $\ln[g(f^q)/g(f^{q-1})]$.

The multiplicity of the degeneracy of $g(f^q)$ and $g(f^{q-1})$ depends on the electronic structure of the ions, which also determines the applicability of the *L*- and *J*-models. The dependence of ln K_p on Z_{An} for both models is shown in Fig. 10*b*. The relationship is the typical strictly regular Ω-relationship, that is the ionic model leads to the regular relationship!

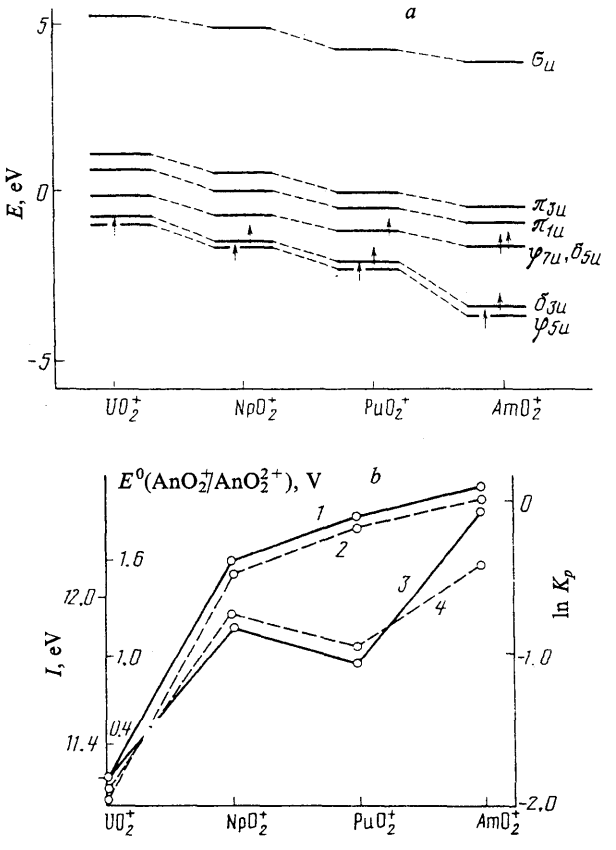


Figure 10. MO diagram for the actinyl ions (*a*) and the dependence of ln K_p [in the *J*-model (curve *1*) and the *L*-model (curve *2*)], the ionisation potentials *I* (curve *3*), and the oxidation potentials E^0 (curve *4*) of the actinyl ions on Z_{An} (*b*).

We can now examine the influence of the crystal field together with spin–orbit coupling. As shown above, the valence 5*f*-AO in the symmetry point group $D_{\infty h}$ are split into δ_u-, φ_u-, π_u-, and σ_u-MO. As a result of spin–orbit coupling, the δ_u- and φ_u-MO are split into δ_{5u}-, φ_{7u}-, δ_{3u}-MO, and π_u into π_{3u} and π_{1u}. Fig. 10*a* shows the filling of these MO with electrons for the actinoyl ions AnO_2^+: $UO_2^+ - \varphi_{5u}^1$; $NpO_2^+ - \varphi_{5u}^1$; $PuO_2^+ - \varphi_{5u}^1\delta_{3u}^1(\varphi_{7u}\delta_{5u})^1$; $AmO_2^+ - \varphi_{5u}^1\delta_{3u}^1(\varphi_{7u}\delta_{5u})^2$. The energy distance between the φ_{5u}- and δ_{3u}-MO is determined mainly by the spin–orbit effect for the free ions, since they are almost pure 5*f*-levels, and the splitting of the π_u-levels is due to the effects of the crystal field and the spin–orbit coupling (CF + SOC) resulting from the considerable mixing with the 2*p*-AO of the oxygen atoms. As a result, the energy distance Δ_1 between the φ_{5u}- and δ_{3u}-MO in AnO_2^+ is about 1500 cm^{-1}, while the distance Δ_2 between the δ_{3u}- and $\varphi_{7u}\delta_{5u}$-MO is greater, and amounts to about 6000 cm^{-1}. In accordance with the scheme adopted for the filling of the MO by electrons and the values of Δ_1 and Δ_2, the change in the ionisation potentials of the actinoyl ions is irregular (Fig. 10*b*); the so-called *N*-relationship is observed. This analysis reveals the reasons for the appearance of a stepwise relationship of the *N*-type. Since the main energy contribution to the oxidation potential $E^0(AnO_2^+/AnO_2^{2+})$ for the chemical reaction $AnO_2^+ \rightarrow AnO_2^{2+} + e$ is associated with the removal of the electron from the AnO_2^+ ion, the corresponding ionisation potentials and the oxidation potential change in the same sense (Fig. 10*b*).

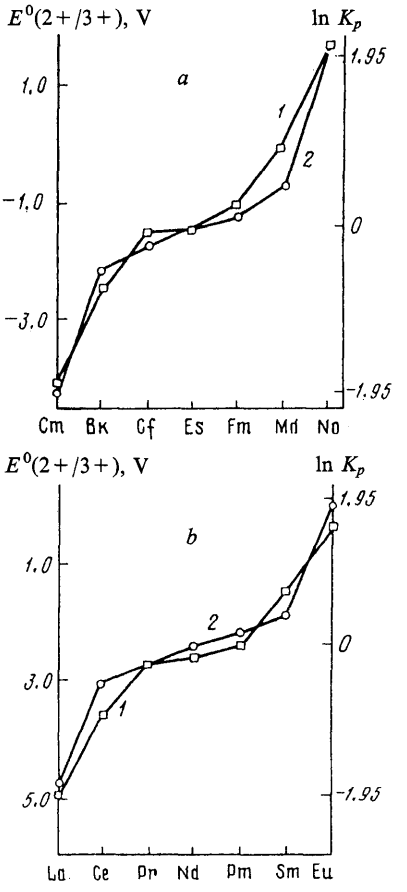


Figure 11. Regular dependence of the potentials $E^0(2+/3+)$ on Z_{An} (*a*) and Z_{Ln} (*b*) (curves *1*), resulting from weak crystal fields and relativistic effects; two Ω-type relationships can be distinguished in each half of the series; the theoretical dependence of ln K_p on *Z* is also given (curves *2*).

Thus when account is taken of strong crystal fields and spin–orbit effects, the Ω-type regular relationship ($K_p - Z_{An}$) in the *L*- or *J*-models becomes an irregular relationship of the *N*-type ($I - Z_{An}$, $E^0 - Z_{An}$).

In other words, it can be stated that the **irregular nature of the dependence of E^0 on the atomic number of the actinide is due largely to strong crystal field and spin–orbit effects.** The opposite is also true: **for weak crystal field and spin–orbit effects, the dependence of E^0 on Z_{An} is regular, of the Ω-type,** like the dependence of K_p on Z_{An}. This is the case for compounds with the electron configurations f^1, f^2, f^3, and f^4 (Fig. 11).

Thus the principal effects responsible for the anomalous properties of the heavy elements are relativistic contraction, spin–orbit splitting, and self-consistent interaction of the orbitals. Relativistic contraction in the case of the *s*-electrons, which have a low density next to the nucleus, leads to a decrease in the radii and an increase in the ionisation potentials of the corresponding ions.

Relativistic effects influence the *p*-AO in the same direction as the *s*-AO, but to a much smaller extent. Finally, relativistic effects influence the *d*- and *f*-electrons in the opposite direction, that is the radii increase and the ionisation potentials decrease. In other words, for an electron configuration $f^q ds^2$ the relativistic effects make the 7*s*-AO more compact and strongly bound, and the 6*d*- and 5*f*-AO more diffuse and weakly bound. In the atom, the relativistic effects for the 5*f*-, 6*d*-, and 7*s*-AO partly compensate one another.

The compounds of actinides in lower oxidation states (3+ and 4+) are practically ionic. This means that in these states the $6d7s^2$-electrons of the actinide are transferred to the ligands, and the 5*f*-electrons are non-bonding. The relativistic effects and crystal field effects increase with increase in the oxidation state.

These postulates can be verified from the values of the redox potentials. In the chemistry of the *f*-elements it is possible to consider two limiting cases: the actinyl and actinoyl ions (strong crystal fields and spin–orbit effects) and the lanthanides and actinides in lower oxidation states 2+ and 3+ (weak crystal fields and spin–orbit effects). Thus in accordance with this approach the oxidation potentials $E^0(2+/3+)$ for the lanthanides and actinides (Figs. 11*a* and 11*b*), with increase in the atomic number of the actinide or lanthanide, change regularly in accordance with the theoretical dependence of ln K_p on Z_{An}. Each half of the series in Fig. 11 shows two relationships of the Ω-type on both the experimental and the theoretical curves. The potentials $E^0(2+/3+)$ for La, Ce, Pr, and Cm were estimated by us, and those for Pm, Bk, Cf, Es, Fm, Md, No [171] and Nd, Sm, Eu [172] were taken from published data. These relationships confirm that the anomalous behaviour of the redox potentials $E^0(AnO_2^{2+}/AnO_2^{+})$ corresponding to high oxidation states is due to strong relativistic effects and strong crystal fields.

These conclusions can be verified from the values of the redox potentials $E^0(3+/4+)$ for the actinides. These potentials have been published.[173] Fig. 12*a* gives the relationships for the measured redox potentials and ln K_p, calculated using the model. Fig. 12 shows that the trends in the changes in E^0 and ln K_p from thorium to curium are identical.

For the actinides with oxidation states of 5+ and 4+, the regular dependence of the redox potentials on Z_{An} breaks down. This is related to the formation in acidic solutions of $PaOOH^{2+}$ and AnO_2^{+} (An = U, Np, Pu, Am) from Am^{4+}.[173] The dependence of $E^0(4+/5+)$ on Z_{An} is shown in Fig. 12*b*. In accordance with relativistic X_α-SW calculations for the AnO_2^{+} ions, the last occupied MO in the ions UO_2^{+}, NpO_2^{+}, PuO_2^{+}, and AmO_2^{+} are the orbitals δ_{3u}^1, $(\varphi_{7u}\delta_{5u})^1$, $(\varphi_{7u}\delta_{5u})^2$, and π_{1u}^1 respectively. The energies of these MO can be regarded as providing a measure of the electron affinity (A) of the actinoyl ions. The dependence of A on Z_{An} for these ions is shown in Fig. 12*b*.

The energies of the last occupidd MO in the actinoyl ions and the corresponding redox potentials $E^0(4+/5+)$ increase regularly with increase in Z_{An} for An = U, Np, and Pu, and then decrease for americium. The partly occupied low-lying levels in the actinoyl ions form three groups: $\varphi_{5u}\delta_{3u}$, $\varphi_{7u}\delta_{5u}$, $3\pi_{1u}3\pi_{3u}$. The last level σ_u lies fairly high. Of the three groups of levels, the first two are practically 5*f*-levels, but in the third group of levels there is extensive mixing of 5*f*- and 2*p*-AO.

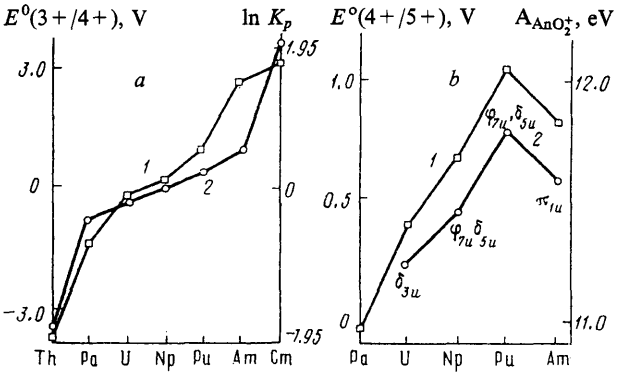


Figure 12. Regular dependence of the redox potentials $E^0(3+/4+)$ for the actinides from Th to Cm, showing agreement with the theoretically expected dependence of ln K on Z (*a*), and the deviation from regularity of the theoretical potentials $E^0(4+/5+)$, corresponding to the change in the electron affinity A (*b*).

The reduction of the actinoyl ions of uranium, neptunium, and plutonium involves the first two groups of levels, and that of americium involves the third group. The replacement of the purely actinide levels taking part in the reduction by levels of mixed character is responsible for the irregular change in the redox potentials (Fig. 12*b*). The correlation between $E^0(4+/5+)$ and A underlines the correctness of the chosen model for explaining the dependence of the redox potentials on Z_{An} within the X_α-SW method.

The same approach can be used to explain the irregular change in $E^0(AnO_2^{2+}/AnO_2^{+})$ with change in Z_{An}. In the oxidation of AnO_2^{+}, the last occupied MO loses an electron; in UO_2^{+} and NpO_2^{+} it belongs to the first group, and in PuO_2^{+} and AmO_2^{+} it belongs to the second group. The change in the levels responsible in a given case for the oxidation again breaks down the regularity of the dependence of E^0 on Z_{an}, but now for plutonium.

Thus the satisfactory qualitative interpretation of the redox properties provides support for the key model assumption that the increasing effects of spin–orbit coupling and the crystal field with increase in the oxidation state are responsible for the chemical anomalies in the redox potentials of the actinides.

We can now consider the changes in the electronic absorption spectra of the actinyl ions. X_α-methods give good agreement with experiment in the range of X-ray photoelectron excitation. It is also possible to obtain satisfactory agreement for the visible range of the spectrum, however. Table 2 gives the energies of the electronic

charge-transfer transitions which we obtained for UO_2^{2+}. Comparison of our data with published data[57,58] shows that for the uranyl ion the calculations give effectively the energy distance between the last occupied and the first unoccupied MO.

Table 2. Energies of the electronic charge-transfer transitions for UO_2^{2+} (cm^{-1}).

Transition	UO_2^{2+}					Transition	$CsUO_2Cl_4$	
	(Ref.123)	Series *					(Ref.57)	(Ref.58)
		(a)	(b)	(c)	(d)			
$3\sigma_u-\varphi_{5u}$	20404	25243	24679	26211	26453	$3\sigma_u-\delta_{3u}$	20095	20406
$3\sigma_u-\delta_{3u}$	22017	26937	26292	27905	28147		20097	21310
$3\delta_u-\varphi_{7u},\delta_{5u}$	28227	33227	32663	34195	34437	$3\sigma_u-\varphi_{5u}$	22026	22410
$3\sigma_u-3\pi_{1u}$	37986	46938	43712	46454	47099		22076	22750
$3\sigma_u-3\pi_{3u}$	40970	47583	46454	49357	49841	$3\sigma_u-\varphi_{7u}$	26197	27719
							26247	27758

*Here and subsequently (in Tables 3–5) the data are given from a series of calculations for the compounds $NaAnO_2Ac_3$ (*a*), $Cs_2AnO_2Cl_4$ (*b*), $RbAnO_2(NO_3)_3$ (*c*), $AnO_2(ClO_4)_2$ (*d*).

Naturally, it is impossible to interpret a large number of lines using a one-electron model. In each case, therefore, the energy of the electron transitions which we obtained corresponds to the weighted-mean energy of several many-electron excited states.

Table 3 gives our calculated energies of the "uranyl-like" transitions for the first four actinyl ions in the actinide series, for compounds with the different types of dependence of R_{An-O} on Z_{An} given earlier. In our calculations, the last occupied orbital is the $3\sigma_u$-MO for UO_2^{2+} and NpO_2^{2+}, and the π_g-MO for PuO_2^{2+} and AmO_2^{2+}, and the "uranyl-like" transitions take place from these MO into unoccupied orbitals of 5*f*-character. The energies of these transitions decrease with increase in the atomic number of the actinide as a result of the lowering of the energy levels of 5*f*-character.

Experimental studies of the neptunyl ion have established that the excited state is described by the electron configuration $3\sigma_u^1\delta_u^1\varphi_u^1$, which leads to the appearance in the spectrum of bands with energies 13918, 16072, 16092, 17967, and 19510 cm^{-1} [70] or 13239, 15239, 15678, 16795, and 19371 cm^{-1}.[71] Similar results were obtained in other studies.[61,62] The charge-transfer bands (E_{CT}) in the actinyl ions correspond to electron transfer for the $3\sigma_u$-MO to the φ_{5u}- and δ_{3u}-MO in the uranyl and neptunyl ions, and from the π_g- to the $\varphi_{7u}\delta_{3u}$, $\varphi_{7u}\delta_{3u}$-MO in the plutonyl and americyl ions respectively. Although the absolute values of E_{CT} differ from the experimental values, the *N*-type of the relationship is clearly revealed. It can be stated that the irregular character of the dependence of E_{CT} on Z_{An} is due to the strong crystal field combined with the spin–orbit effect. Both of these effects are revealed in such properties, different at first sight, as the energies of the uranyl-like transitions and the oxidation potentials, and are responsible for the linear relationship between the potentials $E^0(AnO_2^+/AnO_2^{2+})$ and E_{CT} for these ions. Thus these two properties apparently depend on the same MO.

Table 3. Energies of the "uranyl-like transitions for AnO_2^{2+} (cm^{-1})

Transition	UO_2^{2+}	NpO_2^{2+}	PuO_2^{2+}	AmO_2^{2+}	Series
$3\sigma_u-\varphi_{5u}$	25243	21549	16936*	11533*	(a)
	24679	20485	16291*	11291*	(b)
	26211	22259	18953	13550*	(c)
	26453	23153	19678	15000*	(d)
$3\sigma_u-\delta_{3u}$	26937	23308	18985*	13791*	(a)
	26292	22259	18307*	13468*	(b)
	27905	24437	21049	15726*	(c)
	28147	25009	21775	17259*	(d)
$3\sigma_u-\varphi_{7u},\delta_{5u}$	33227	30485	26937*	22582*	(a)
	32663	29356	26211*	22259*	(b)
	34195	31131	28953	24517*	(c)
	34437	32106	29598	25969*	(d)
$3\sigma_u-3\pi_{1u}$	46938	41212	36534*	30898*	(a)
	43712	39357	35566*	30646*	(b)
	46454	43631	39597	33792*	(c)
	47099	44204	40808	35970*	(d)
$3\sigma_u-3\pi_{3u}$	47583	44276	39921*	34518*	(a)
	46454	42421	38873*	34195*	(b)
	49357	44034	42905	37502*	(c)
	49841	47268	44196	39599*	(d)

Note. Transitions for the π_g-orbital are marked with an asterisk.

In fact, the oxidation potentials $E^0(AnO_2^+/AnO_2^{2+})$ are determined by the ionisation potential of the actinoyl ion $I(AnO_2^+)$ or the electron affinity $A(AnO_2^{2+})$. The values of E_{CT} depend mainly on the electron affinity of the AnO_2^{2+} ions. It is not the whole set of MO, but only individual MO, that make the main contribution to the vlalues of E^0 and E_{CT} and are responsible for the identical (*N*-type) dependence of these properties on Z_{An}.

The classical object for the study of the energy of *f*–*f* transitions is the neptunyl ion, which contains one electron in the φ_{5u}-level. Table 4 compares our calculated energies of the *f*–*f* electron transitions for the neptunyl ion with experimental data,[59,71,73] and Table 5 gives the energies of the *f*–*f* transitions in the actinyl ions. These data indicate that the centres of gravity of bands corresponding to transitions of the same kind are displaced along the actinyl ion series towards an increase in their energies. As noted above, the spectra of the *f*–*f* transitions reflect two trends in the

change in the energies of the MO: the decrease in the splitting of the 5*f*-AO by the crystal field of the ligands along the series, and the increase in their splitting as a result of spin–orbit coupling. Thus in the uranyl ion the splitting of the 5*f*-AO by the crystal field is twice their splitting by spin–orbit coupling, whereas towards the end of the series the two effects are of almost equal magnitude.

Table 4. Energies of the *f*–*f* electron transitions in NpO_2^{2+} compounds (cm^{-1}).

Transition	Calculated for the series				Experiment			
	NpO_2^{2+}				$Cs_2NpO_2Cl_4$		$Cs(NpO_2)(NO_3)_3$	
	(a)	(b)	(c)	(d)	(Ref.59)	(Ref.71)	(Ref.59)	(Ref.73)
$\delta 3_u - \varphi 7_u$	7178	7097	6693	7097	6880	6890	6459	6750
$\delta 3_u - \delta 5_u$	7178	7097	6693	7097	7990	7880	9420	8180
$\delta 3_u - 3\pi 1_u$	17904	17098	19093	19194	17241	17241	17843	18000
$\delta 3_u - 3\pi 3_u$	20969	20153	19597	22259	20080	–	20816	21000

The splitting by the crystal field and spin–orbit coupling is much smaller in the actinoyl ions than in the actinyl ions.[119]

Overall, in the actinyl and actinoyl ions, increase in the atomic number of the actinide displaces transitions of the same kind into the ultra-violet range of the spectrum.

To interpret the redox properties and electronic absorption spectra of the actinyl and actinoyl ions we used individual MO, responsible for the ionisation potentials, their electron affinity, energy transitions, etc. Other properties, for example the thermodynamic properties, depend not on the energy of the last occupied MO but on the energies of the whole set of MO for the compound or ion that is on their sum.

We can write an expression for the standard enthalpy of formation of AnO_2^{2+} using the ionic approximation

$$\Delta H^0(AnO_2^{2+}) = \Delta H^0(An^{6+}, \text{gas}) + A(R_{An^{6+}} + R_{O^{2-}})^{-1} + B, \quad (9)$$

where

$$\Delta H^0(An^{6+}, \text{gas} = \Delta H^0(An, \text{gas}) + \sum_{z=1}^{6} I_z + 15RT. \quad (10)$$

Here, A and B are constants, and $R_{An^{6+}}$ and $R_{O^{2-}}$ the ionic radii of An^{6+} and O^{2-}. The error in the calculation of $\Delta H^0(AnO_2^{2+})$ is due to the neglect of the interaction of the 5*f*-, 6*d*-, and 7*s*-AO with the 2*p*-AO of the oxygen atoms. This is a crude and approximate calculation scheme, so that we shall restrict ourselves to qualitative estimates of the thermodynamic quantities.

The trend in the change in the enthalpies of formation of the actinyl ions is determined by the second term in Eqn. (10), that is by the sum of the ionisation potentials of the actinide atom, and not by the last ionisation potential, as in the case of the redox potentials. The sum of the first two ionisation potentials remains almost unchanged for U, Np, Pu, and Am, and has the values 17.58, 17.58, 17.50, and 17.633 eV respectively. Thus the trend in the change in $\sum_{z=1}^{6} I_z$ is determined by the sum $\sum_{z=3}^{6} I_z$, and that for $\sum_{z=1}^{5} I_z$ is determined

Table 5. Energies of the *f*–*f* electron transitions for AnO_2^{2+} (cm^{-1}).

Transition	NpO_2^{2+} in the series				PuO_2^{2+} in the series				AmO_2^{2+} in the series			
	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
$\varphi 5_u - \delta 3_u$	1758	1774	2178	1855	2048	2016	2097	2097	2258	2178	2178	2258
$\varphi 5_u - \varphi 7_u$	8936	8871	8871	8952	10000	9920	10000	7823	11049	10968	10968	10968
$\varphi 5_u - \delta 5_u$	8936	8871	8871	8952	10000	9920	10000	7823	11049	10968	10968	10968
$\varphi 5_u - 3\pi 1_u$	19662	18872	21371	21049	19598	19280	20646	21130	19356	19356	20243	20967
$\varphi 5_u - 3\pi 3_u$	22727	21937	21775	24114	22985	22582	23953	24517	22985	21904	23953	24598
$\delta 3_u - \varphi 7_u$	7178	7097	6693	7097	7952	7904	7904	7823	8791	8791	8790	8710
$\delta 3_u - \delta 5_u$	7178	7097	6693	7097	7952	7904	7904	7823	8791	8791	8790	8710
$\delta 3_u - 3\pi 5_u$	17904	17098	19093	19194	17549	17259	18549	19033	17098	17178	18065	18711
$\delta 3_u - 3\pi 3_u$	20969	20153	19597	22259	20936	20565	21856	22420	20727	20727	21775	22340

by the sum $\sum_{z=3}^{5} I_z$. From Eqn. (8) we can write the sum of the ionisation potentials $\sum_{z=3}^{5} I_z$ in the form:

$$\sum_{z=3}^{5} I_z = \sum_{z=3}^{5} \ln \frac{2L_z\left(f^{q-1}\right)+1}{2L_z\left(f^{q}\right)+1}, \qquad (11)$$

where the values of $L(f^{q-1})$ and $L(f^q)$ correspond to the reaction

$$\mathrm{An}(f^q) \rightarrow \mathrm{An}(f^{q-1}) + \mathrm{e},$$

and are determined from the values of the normal terms of the actinide ions

	U	Np	Pu	Am
An^{2+}	*I*	*H*	*F*	*S*
An^{3+}	*I*	*I*	*H*	*F*
An^{4+}	*H*	*I*	*I*	*H*
An^{5+}	*F*	*H*	*I*	*I* .

(12)

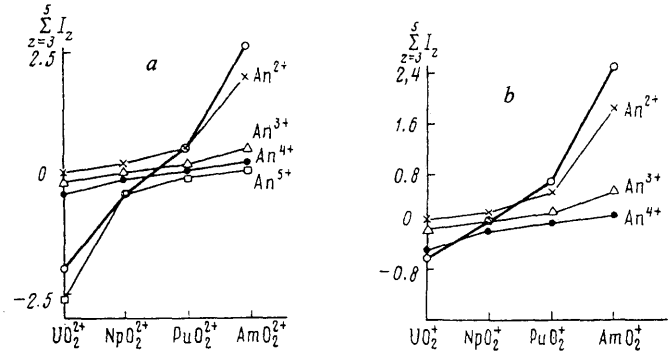


Figure 13. Qualitative trend in the change in the dependence of the sum of the ionisation potentials of the actinide atoms An^{5+} [Eqn. (11)] $\sum_{z=3}^{5} I_z$ on Z_{An}, determining the change in the enthalpy of formation of the actinyl (*a*) and actinoyl (*b*) ions (thick line); the thin lines show the trend in the change in the successive ionisation potentials of An^{2+}, An^{3+}, etc.

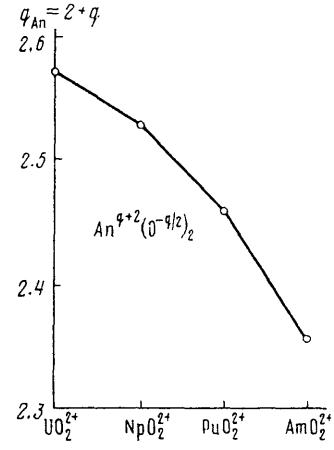


Figure 14. Dependence of the effective charges in the actinyl ions on the atomic number of the actinide.

The trends in the changes in the separate ionisation potentials of An^{2+}, An^{3+}, etc., and also their sums, determined from Eqn. (11) with allowance for the values of the normal terms, with change in the atomic number of the actinide are shown in Fig. 13. The complete analogy between the experimental relationship for the enthalpies of formation (Fig. 6) and the theoretical relationship (Fig. 13) shows that the trend in the change in the enthalpies of formation is determined by the sum of the first six ionisation potentials for the actinyl ions, and by the sum of five ionisation potentials for the actinoyl ions. In the sum of the ionisation potentials, the spin–orbit contribution is small compared with the electron–electron interaction energy, so that it does not determine the trend in the change in properties, in contrast to the redox potentials, where relativistic corrections make a significant contribution to the values.

It is of interest to consider the relationship obtained for the redox properties by examining them using the purely ionic model, that is using not the ionisation potentials of the actinoyl ions $I(AnO_2^+)$ but the ionisation potentials of the free ions, namely $U^{5+}(^2F,f^1)$, $Np^{5+}(^3H,f^2)$, $Pu^{5+}(^4I,f^3)$, and $Am^{5+}(^5I,f^4)$. The dependence of the redox potentials calculated in the ionic approximation on Z_{An} will be regular, and of the Ω-type and not the *N*-type, as observed experimentally.

Fig. 14 shows the dependence of the effective charges on the actinide ions (An = U, Np, Pu, and Am) on Z_{An}. The relationship is of the Ω-type. For the actinyl ions the larger the distance R_{An-O}, the smaller the effective charge on the actinide atom, that is for an infinitely large distance R_{An-O} the charge on An tends to +2, corresponding to the presence of the free actinide ion An^{2+} and oxygen atoms.

From the electron density distribution in the actinyl ions it follows that the effective electron configuration of the actinide atoms in the bonding levels is $5f^{2.6-3.2}6d^1$. This electron configuration corresponds approximately to a double bond in the uranyl ion. The 6*s*- and 6*p*-AO will increase the U–O bond order slightly.[40]

It may be concluded that the Ω-type dependence of q_{An} on Z_{An} for the actinyl ions from UO_2^{2+} to AmO_2^{2+} will lead to an Ω-type dependence of R_{An-O} on Z_{An} (see Fig. 1). At the same time, there is a linear relationship between q_{An} and R_{An-O}. This conclusion applies either to the free ions AnO_2^{2+} or to compounds AnO_2X_y in which the ligands X do not have a significant influence on the electronic structure of the actinyl ions.

If, as is usually done in chemistry, the reactivity of ions is characterised by the ionisation potentials and electron affinity, and the electronegativity is defined as $F = I + A$, it is found that the values of I, A, and F change irregularly according to a relationship of the N-type (Fig. 15), that is a relationship of the type already encountered for various properties of the actinyl and actinoyl ions, such as the internuclear distances, bond force constants, molecular polarisabilities, refractive index, etc. Since the irregular relationships for I, A, and F are due to relativistic effects and the crystal field, it may be concluded that the properties of the N-type of the actinyl complexes determined by these parameters will also be due to these effects. The N-type of relationship is determined by the electronic structure of the actinyl ions, and the ligands X increase or decrease the strength of this type of relationship, by donating or accepting electron density. Here, there are two possibilities.

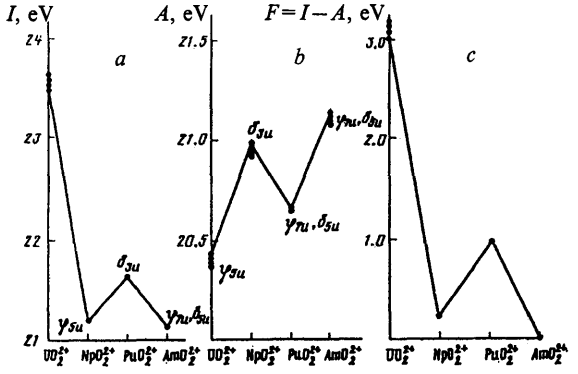


Figure 15. Irregular N-shaped change in the ionisation potentials (a), electron affinity (b), and electronegativity (c) of the actinyl ions on Z_{An}; the MO responsible for the change in these quantities in each ion are shown.

1. The ligands X in the equatorial plane decrease the strength of the An−O bond, which becomes more ionic, and the effects of the crystal field decrease. The L-model begins to "operate". The dependence of the properties on the atomic number of the actinide is of the Ω-type.

2. The ligands X increase the strength of the An−O bond, the effects of the crystal field increase, and the dependence of the properties on Z_{An} remains of the N-type, as for the free AnO_2^{2+} ions.

If it is assumed that complex formation by AnO_2^{2+} ions with ligands X involves the reaction of unoccupied and partly occupied levels of the 5f-type, and also occupied σ- and π-levels mainly of oxygen atoms, it is possible to explain why the enthalpy of formation of the complexes AnO_2X_y will have an extremal value on going from the neptunyl to the plutonyl compounds. This also applies to the enthalpy of extraction. The strong crystal field, combined with the spin−orbit effect, also determines these important chemical characteristics, giving a dependence of the N-type. If the An−O bonds are sufficiently weakened by the ligands X, these properties change according to a relationship of the Ω-type.

The effects of spin−orbit coupling and the crystal field divide the actinyl ions of the first half of the series into two tetrads sharing the americyl ion: UO_2^{2+}, NpO_2^{2+}, PuO_2^{2+}, AmO_2^{2+} and AmO_2^{2+}, CmO_2^{2+}, BkO_2^{2+}, CfO_2^{2+}. In the approximation of free sextuply-charged actinide ions, this division corresponds to the normal terms $^1S_0$, $^2F_{5/2}$, $^3H_4$, $^4I_{9/2}$ for the first tetrad, and $^4I_{9/2}$, $^3H_4$, $^2F_{5/2}$, $^1S_0$ for the second tetrad.

Similarly, the actinoyl ions form two tetrads, from PaO_2^+ to PuO_2^+ and from PuO_2^+ to BkO_2^+.

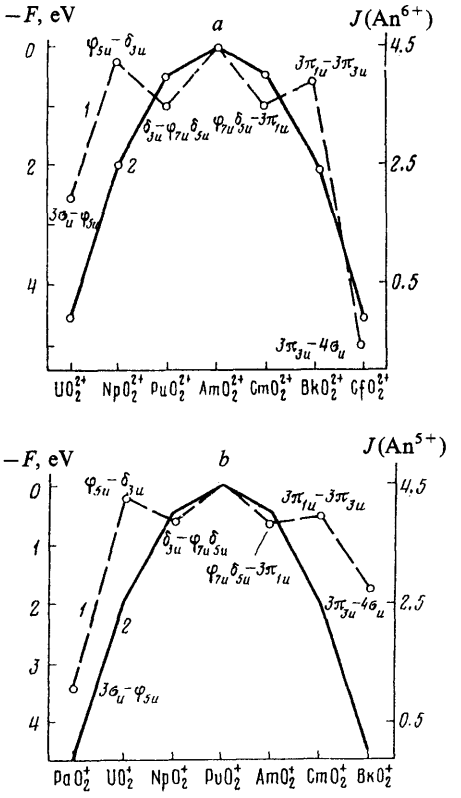


Figure 16. Dependence of the electronegativity $F = -I + A$ for the actinyl (a) and actinoyl (b) ions (curve 1) and the quantum numbers J (curve 2) for the normal terms of the sextuply-charged (a) and quintuply-charged (b) ions on Z_{An}; the MO determining the quantities I and A are shown on the dependence of F on Z for each ion.

Figure 16 shows the dependence of the electronegativities of the ions AnO_2^{2+} (Fig. 16a) and AnO_2^+ (Fig. 16b) on Z_{An}. The dependence of the quantum numbers J for the free sextuply-charged An^{6+} and quintuply-charged An^{5+} ions on the atomic number of the actinide is given for comparison. The "saw-tooth" dependence of F on Z_{an} for the actinyl and actinoyl ions has the general character of bell-shaped curves and is similar to the dependence of the quantum numbers J on Z_{An} for the quintuply- and sextuply-charged ions. This means that there should be a qualitative

correlation between various properties of the actinyl and actinoyl ions and the quantum numbers J for the free ions An^{6+} and An^{5+}. These are tetrads in the J-model, but not in the L-model. It follows from Fig. 16 that the values of F in both tetrads change with increase in Z_{An} according to an N-relationship. Curves of this type are observed when the properties of the actinyl and actinoyl ions depend on definite MO, and not on the entire set of MO as a whole. Thus the electronegativity of the uranyl ion is determined by the energy corresponding to the charge-transfer band $F_{UO_2^{2+}} = E_{3\sigma_u} - E_{\varphi_{5u}}$; the electronegativity of the neptunyl ion is smaller, since it depends on the energy of spin–orbit splitting $F_{NpO_2^{2+}} = E_{\varphi_{5u}} - E_{\delta_{3u}} \simeq \zeta$; for the plutonyl ion, the value is $E_{PuO_2^{2+}} = E_{\delta_{3u}} - E_{\varphi_{7u},\delta_{3u}} \simeq 2.5\zeta$; finally, for AmO_2^{2+}, $F \simeq 0$, since the degenerate φ_{7u},δ_{5u}-MO contains one electron. The irregular $F_{AnO_2^{2+}}$ relationship is responsible for the appearance of relationships of the N-type in each of the tetrads from the uranyl to the americyl ion and from the americyl to the curyl ion.

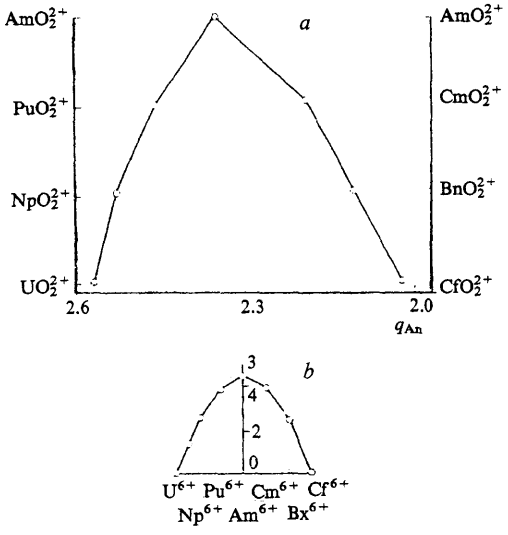


Figure 17. Dependence of the effective charges on the actinide atoms in the actinyl ions (*a*) and the corresponding dependence of the quantum numbers J of the total angular momenta for the sextuply-charged ions An^{6+} in the ground electronic state (*b*) on Z_{An}.

In the so-called summative properties which depend on all the MO, such as the electron density distribution, a relationship of the Ω-type is observed. This type of relationship is shown in Fig. 17*a* for the effective charges on the actinide atoms in the actinyl ions. The two tetrads for the change in q_{An} are completely analogous to the two tetrads for the values of the quantum numbers J of the normal terms of the sextuply-charged actinide ions in Fig. 17*b*.

IV. Summary

Before summarising the interpretation of the physicochemical properties of the actinyl and actinoyl ions based on X_α-SW calculations, we ask the question: is the chemistry of compounds of this class enriched by new chemical ideas as a result of these calculations, or do they provide a basis only for the quantitative interpretation of the properties? We have never been under the illusion that calculations for a particular molecule, no matter how well they are carried out, that is using the entire arsenal of computer techniques, will open the gates of the unknown. We have emphasised this idea many times (see for example our earlier review[174]). The calculation for a series of molecules or ions of the same type, as in the present case, has made it possible to determine the reasons for the irregular change in a number of properties along the series, and this cannot be done by restricting the calculation to one ion, for example the uranyl ion, as has been the practice until now. The calculations should not be restricted to the simple Hückel method, since it has been found that the irregularity is a manifestation of relativistic effects combined with the crystal field effect. X_α-SW calculations have made it possible to understand why some properties change regularly while others change irregularly.

The division of MO into fragments is not a new idea in chemistry. In the case of the actinide compounds, however, there is a characteristic specific reason for this division, related to the division of the AO of the actinide atoms into three groups, according to the energy values: $6s + 6p$, $5f$, and $6d + 7s$. This gives a characteristic fragmented system of energy levels; in the fragments, individual MO of the same type have similar AO compositions.

Finally, there is considerable debate in the literature on the existence of the tetrad and double–double effects and their interpretation and limits of applicability.[47,80–84] In fact, at first sight it appears strange that such "down to earth" properties of the compounds of the lanthanides and actinides as the extraction constants or complex-formation constants of the f-ions correlate with the quantum numbers L and J of the normal terms, not to mention that there is no difference between them, that is the logarithms of the extraction coefficients of the lanthanides for a given extracting agent in some sources correlate with the quantum numbers J and in others with L.[84,85] By using the methods of statistical physics combined with calculations for the entire series of observed and hypothetical ions AnO_2^{2+} and AnO_2^{+}, we have been able for the first time to go beyond simple "property–quantum number" correlations and have been able to show why and when these correlations are significant, and also that these correlations determine the trend in the change in properties, but no more. Without a series of calculations it was impossible to suggest (and nobody has done it!) that the effective charges on the actinide ions in actinyl compounds obey the tetrad relationship. Moreover, it can be stated that in isovalent compounds of the actinide series, for example in $AnHal_6$, where An = U, Np, ..., Bk, the relationships observed will be of the same type as for the actinyl ions (strictly regular, regular, and irregular relationships). These questions will be examined in later papers, but here we point out that the relationship is general and provide an explanation. Thus the problem of determining the electronic structure of the actinyl and actinoyl ions, formulated in the Introduction, can be regarded as solved. In the carrying out of systematic series of calculations for systems of the same type we see the optimum use of the methods of computational quantum chemistry for analysing experimentally observed relationships and predicting new ones.

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