

S 50. *The Position of the Cis- and Trans-uranic Elements in the Periodic System: Uranides or Actinides?*

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Reasons are advanced against the classification of the cis-uranic elements in a new rare-earth series, the actinides.

THE question of the existence of a rare-earth series in the seventh period and its classification as an actinide, thoride, protoactinide, or uranide series must be considered from the standpoint of the general evolution of the chemical properties of the elements in the whole Periodic System, and not only in relation to the characteristics of the seventh period. Now that all the elements are known, we are able to understand fairly thoroughly the nature of the periodicity and the very complex relationships which exist between their properties and structures. In particular, we see the danger of predicting the behaviour of an element or a group of elements by analogy and extrapolation only; when not based on experimental facts, completely erroneous conclusions may be drawn. Illustrations of this statement are to be found all through the Periodic System, particularly at its upper end.

We shall begin with the element of atomic number 79, *i.e.*, gold. Its valency anomaly is well known: although belonging to the first group, it is most stable in the trivalent state. Its neighbour, mercury, unlike the homologues zinc and cadmium, has numerous stable univalent compounds; further, extrapolation of the melting points of zinc and cadmium does not indicate that mercury is liquid at room temperature.

Thallium, an element of the third group, is not only most stable in the univalent compounds, but its behaviour in this oxidation state is very similar to that of the alkali metals. With regard to lead, Marie Curie said, not without reason, that it is an alkaline earth which "got into the wrong case".

The chemical properties of polonium are known only on the tracer scale, but what we know could not have been predicted merely from the extrapolation of the properties of selenium and tellurium. Indeed, for some years it was believed that the polonium discovered by the Curies differed from the eka-tellurium of Marckwald. Finally, though the properties of astatine are as yet little known, we may conclude from the recent paper by Johnson, Leininger, and Segre (*J. Chem. Physics*, 1949, **17**, 1) that this element is far from being an orthodox halogen.

Of course, these apparent anomalies can be more or less well explained by the electronic structures of the atoms, and, now that they are known, they can be understood within the scheme of the general evolution of properties in the groups and in the periods. The great and continuing usefulness of the Periodic System consists in the fact that it expresses this variation so well: whilst, on the one hand, it enables us to arrange the elements of neighbouring fundamental properties in chemical groups and families, it also sums up the individual characteristics of each element inside its group. The system, however, would lose its significance if elements very different chemically were classified in the same family. This is the error committed by the protagonists of the actinide hypothesis.

Let us examine the seventh period. The group relationship is shown rather better in this than in the previous period. This is well established for francium and radium, and is also nearly true for actinium *vis-à-vis* lanthanum, although it is not quite clear why in some fractionated precipitations actinium does not accompany lanthanum but is found between neodymium and samarium. Boussières and the author (XIth International Congress of Chemistry, London, July, 1947) have shown that thorium is a true homologue of zirconium and hafnium, and that protoactinium is similarly the homologue of niobium and tantalum. This conclusion is drawn from a consideration of the tendencies to hydrolysis and complex formation, basicity, and acidity, stability of peroxides, electrochemical behaviour, etc.

The very recent discovery of lower valencies of protoactinium (Haissinsky and Boussières, *Compt. rend.*, 1948, **226**, 573) and thorium (Hayek and Rehner, *Experientia*, 1949, **5**, 114; Anderson and D'Eye, this vol., p. S 244) does not alter this conclusion. The great instability of its tri-iodide and its metallic aspect show, as pointed out independently by Hayek and Rehner and by Anderson and D'Eye (*loc. cit.*), a similarity with the lower halides of zirconium and hafnium, but marked differences from cerium tri-iodide. The analogies between uranium and the other elements of the sixth group, molybdenum and tungsten, are also well known, though some differences also exist.

Not only are actinium, thorium, tantalum, and uranium true homologous members of their respective groups, but in their most stable oxidation state they are very different from one another, as different as it is possible for any four neighbouring elements to be. This fact is decisive, and largely sufficient for the rejection of any classification which endeavours to place these elements in the same chemical group. Radiochemists, who encounter so much difficulty in separating natural protoactinium from its homologue tantalum and who easily separate it from thorium and uranium, could never admit such a classification. The classification of the three cis-uranic elements with uranium in a new rare-earth series, called actinides, is not only contrary to the historical development and to the chemical significance of the first rare-earth series, the lanthanides, but is also didactically wrong* and induces an unnecessary perturbation in the Periodic System.

Let us now consider the facts which led Seaborg to support the actinide hypothesis. The three elements uranium, neptunium, and plutonium can exist in the valency states 6, 5, 4, and 3, the stability of the valencies 4 and 3 increasing from uranium to plutonium. Then follow americium with valencies 3, 4, and 5,† the first being the most stable, and curium with the valency 3 only.

There is no analogy with the corresponding elements of the lanthanide series, which from lanthanum to gadolinium have normally only the stable valency 3, except for cerium, which has also the unstable valency 4, and praseodymium with the valency 4 in the oxide (but not in solution). The lower valency 2 is known for samarium and europium.

From a purely chemical point of view, the striking similarity of the properties of uranium, neptunium, and plutonium, recall the triads of the eighth column. But as these elements are followed by americium and curium which have only lower valencies, one might think that we have here a pentad of transition elements similar to the triads, where too, the higher valency diminishes from left to right. Quantum mechanics, however, predicts the appearance of 5f electrons somewhere in the neighbourhood of uranium. Because of the statistical character of the calculations carried out on a small number of particles of the electronic gas, it is known that the precision of the theory is poor. For the lanthanides, Goeppert-Mayer (*Physical Review*, 1941, **60**, 184) found that the first 4f electron should appear in the neodymium atom (instead of cerium). For the seventh period, the theoretical results vary between element 91 (*idem, ibid.*) and 93 (Wu and Goudsmith, *ibid.*, 1933, **43**, 496). By stating, then, that there exists in this period a uranide series, we satisfy both the chemical evidence and the general theoretical conclusions. We thus avoid any confusion between very different elements and between the new series and the lanthanides, the latter being, in any case, very different from the former.

The hypothesis of a thoride series should be eliminated on the same grounds. Its existence does not seem probable if we examine the variation of the quadrivalency stability in the

* In a recent paper, Purkayastra (*Nucleonics*, 1948, **3**, No. 5) says that thorium, protoactinium, and uranium are not well defined as higher homologues of hafnium, tantalum, and tungsten. This statement is, of course, contradicted by chemical evidence, but is perhaps a logical consequence of the actinide hypothesis as understood by this author, who sees in the co-precipitation of protoactinium with zirconium as phosphate and with thorium as oxalate an indication of its valency!

† The valency 4 for the highest oxidation state of americium has been claimed in all American publications until today; but Dr. Connick (this vol., p. S 237) has announced that the higher valency is 5. It seems that the existence of other, unstable, valencies of curium cannot be excluded.

seventh period. This variation is given schematically below, where the number of the lines increases with the stability :

Th	Pa	U	Np	Pu	Am ?	Cm ?
_____?	_____	_____	_____	_____?
_____			_____		
_____				_____		

The existence of a protoactinide series could more easily be compatible with the chemical evidence, but such an hypothesis is unnecessary.

At the XIth International Congress of Chemistry, Dr. Maddock remarked that the elements can be classified according to either their chemical properties or their electronic structures : the two methods generally lead to the same results, but at the end of the Periodic System they may give alternative arrangements. Since theory cannot yet decide with sufficient accuracy as to the location of the *5f* electrons, Maddock's remark would signify that, although the chemical evidence is contrary to the existence of a homogeneous actinide series, analogous to the lanthanides, yet physical facts would be favourable to the appearance of the first *5f* electron in thorium. If this is so, since we are dealing with the Periodic System, which is essentially a chemical classification, there is no reason for the introduction of an actinide series ; but let us examine the physical facts.

The principal methods used for the determination of the electronic structures in the seventh period are measurements of *X*-ray terms, optical absorption and emission spectra, and magnetic susceptibilities. The work of Sugiura and Urey (*Danske Vid. Akad., Math.-fys. Medd.*, 1926, VII, No. 13), giving a classical quantum interpretation of the *X*-ray terms of thorium and uranium, is probably the first made in this direction. They concluded that the *5f* electrons do not appear before element 95. But according to Starke (*Naturwiss.*, 1947, **34**, 62), Russel (unpublished work) found from the *X*-ray spectrum that the *f* levels of uranium are deeper than those of the *d* levels. Other authors (Ephraim and Mezener, *Helv. Chim. Acta*, 1933, **16**, 1257; Goldschmidt, *Fra Fysik. Verden*, 1942, **3**, 179) see in the absorption spectra sharp band structure given by compounds of U(IV) and similar to that for the rare earths, an indication of the existence of thoride series. Starke (*Z. anorg. Chem.*, 1943, **251**, 251), however, noted that the argument is not convincing, since compounds of the iron group give the same type of absorption spectra.* As for the emission spectra, it is known (MacNally, *J. Opt. Soc. Amer.*, 1942, **32**, 334; De Bruin, Klinkenberg, and Schuurmans, *Z. Physik.*, 1943, **121**, 667; 1944, **122**, 23; Meggers, *Science*, 1947, **105**, 514) that in the case of thorium, the fundamental terms do not correspond to *f* electrons. On the contrary, the results of two groups of spectroscopists (Kiess, Humphreys, and Laun, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 57; Schuurmans, *Physica*, 1946, **11**, 419) seem to indicate the presence of three *5f* electrons in the uranium atom. Kiess, Humphreys, and Laun (*loc. cit.*) even affirm that the structure of the uranium spectrum is similar to that of neodymium. This very surprising result is contradicted by previous measurements of magnetic susceptibilities by several authors (Bose and Bhar, *Z. Physik*, 1928, **48**, 716; Sucksmith, *Phil. Mag.*, 1932, **14**, 1115; Lawrence, *J. Amer. Chem. Soc.*, 1934, **56**, 776; Haraldsen and Bakken, *Naturwiss.*, 1940, **28**, 127). These experiments lead to the conclusion that the valency electrons of uranium are $7s^2 6d^4$. The difficulties of interpretation of such complex spectra as those of uranium are well known, and perhaps it would be better to await confirmation of these results, which are considered by Kiess *et al.* as preliminary. Uranium and neodymium being chemically very different, such a confirmation would give a very good illustration of the lack of direct relationships between electronic structure and chemical character in this part of the Periodic System. But even then, the presence of three *5f* electrons in uranium does not necessarily signify that protoactinium has two and thorium one *5f* electron. Indeed, other cases are known, where two or three electrons of a given group appear suddenly together in an atom; e.g., $^{76}\text{Os } 5d^6 6s^2$, $^{77}\text{Ir } 5d^9$.

Further research is certainly necessary in order to establish the electronic distribution in the outer shells of the uranides and of their neighbours. But the author agrees with Seaborg (*Ind. Eng. Chem., News Edn.*, 1946, **24**, 1197) that "sometimes it may be something of an academic matter to assign electrons to the *5f* or *6d* shells". For the chemical point of view, however, the differences between the cis- and the trans-uranic elements are too well marked for their inclusion in one and the same series.

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* For the same reason, the close values for the ionic radii of thorium and U(IV), pointed out by Goldschmidt (*loc. cit.*) as favourable to the thorides, are not decisive, as he himself noted.