Electron Configurations of "Rare-Earth" Elements

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THE DISCOVERY OF FISSION OF URANIUM atoms by Hahn and Strassmann in 1939 has led to the most spectacular scientific developments in the world's history. Direct consequences were atomic energy release by chain reactions, culminating in the atomic bomb of 1945, and neutron sources of fantastic intensity with which it has been possible to manufacture significant amounts of new elements and isotopes. The artificial elements of greatest interest are the transuranic elements, 93 (neptunium), 94 (plutonium), 95 (americium), and 96 (curium), since both theoretical calculations and chemical speculations have been made as to the probability of 5*f*-type electrons appearing in the 7th period of the Periodic Table. The purpose of the present discussion is to review some of these suggestions and to draw attention to the spectroscopic evidence bearing on this question.

In 1926 Sugiura and Urey (*6*), from quantum-theoretical calculations of central fields based on X-ray terms, were "led to the expectation that levels corresponding to the interior 5_4 electrons should not appear before an element with atomic number 95."

In 1933 Wu and Goudsmit (*7*) calculated from Schrödinger's equation the energies of various electrons of atoms and ions built upon the radon core and concluded that "beginning with element 93 we have to consider the sixfold ionized atom to obtain the ion with the radon core and in this ion the 5*f* is certainly the lowest level. This makes it very probable that the neutral atom 93 in its normal state contains at least one 5*f* electron."

In 1941 Mayer (*3*), from calculations of the eigen functions of the 4*f* and 5*f* electrons, concluded that "the calculations for the rare-earth group agree moderately well with experimental facts. The theory would predict that the 4*f* orbits start to be filled at $Z = 61$, or $Z = 60$, at the earliest. Actually the first 4*f* electron occurs at $Z = 58$. In the neighborhood of $Z = 92$ the theory predicts occurrence of a second rare-earth group; the first filled 5*f* level should occur at $Z = 91$ or 92. Experimentally it appears that uranium does not yet possess a 5*f* electron. Inaccuracies of a few units in Z are to be expected in a calculation based on the statistical model."

Quantum theory, wave mechanics, and quantum mechanics have thus far failed to yield an accurate solution of this problem.

In 1940 McMillan and Abelson (*2*) announced the discovery of radioactive element 93 and stated that "the new element has little if any resemblance to its homologue rhenium. This fact together with the great similarity to uranium suggests that there may be a second 'rare-earth' group of similar elements starting with uranium."

In 1946 Seaborg (*5*), after reviewing the oxidation states of the transuranic elements, said that "the evidence strongly indicates that we are dealing here with a transition series of elements in which the 5*f* electron shell is being filled in a manner similar to the filling of the 4*f* electron shell in the well-known rare-earth series. Apparently this new transition series begins with actinium in the same sense that the rare-earth series begins with lanthanum, and, although the first elements in the heavy series exhibit the property of undergoing oxidation to higher states up to a maximum oxidation state of VI, the tendency in the later members of the series is to have a stable lower oxidation state, such as the III state. The most important criterion for arranging the heavy elements in this series is the probable presence of seven 5*f* electrons (analogous to the stable gadolinium structure) in tripositive curium (element 96), rather than the presence of the first 5*f* electron in thorium. In fact, there might not be any such electrons in thorium with, for example, their first appearance in protoactinium (two 5*f* electrons) or in uranium (three 5*f* electrons); and, of course, it is recognized that the 5*f* and 6*d* shells of the elements in this region lie so close together that the energy necessary for the shift from one shell to the other may in some cases be within the range of chemical binding energies. Previous to the discovery of the transuranium elements, it was almost the universal attitude that a simple filling of the 6*d* shell of electrons was taking place (*i.e.* in the elements of atomic numbers 89–92), and practically all the standard works and textbooks on chemistry and physics adopted this view. It was possible to come definitely to this other view only as a result of the study of the transuranium elements. However, it should be pointed out that a number of people have previously made the suggestion that the 5*f* electron shell begins to be filled in this region, just before or after uranium. It is beyond the scope of the present discussion to review these suggestions."

The chemical evidence proves conclusively that elements 93, 94, 95, and 96 are not homologues, respectively, of elements 75 (rhenium), 76 (osmium), 77 (iridium), and 78 (platinum), but beyond this there is no chemical proof that the heaviest elements contain 5*f* electrons except by analogy with the rare earths 58 (cerium) to 64 (gadolinium), which are known from spectroscopic (not chemical) evidence to contain 4*f* electrons. Chemists usually include 21 (scandium), 39 (yttrium), and 57 (lanthanum) in the rare earths because they exhibit similar properties (excepting spectroscopic) and oxidation states. Spectroscopists do not regard these three elements as true rare earths because they have no *f*-type electrons in their normal configurations. The valence electrons of these elements are d^1s^2 or d^2s^1. As a matter of fact, there is no direct chemical evidence for the existence of *f*-type electrons in any atoms. In the 4*f*-type rare earths (except 58 Ce) the 4*f* electrons are completely submerged in the N shell; they are inactive as valence bonds compared with the less firmly bound 5*d* electrons in the O shell or 6*s* electrons in the P shell. In the 5*f*-type rare earths the differences between binding forces on 5*f*, 6*d*, and 7*s* electrons are less, and again there is no chemical evidence for distinguishing between them. All that can be said is that, because 96 Cm in period 7 shows only tripositive valence, it may be assumed that some electrons (presumably 5*f*) are submerged and inactive, analogous to the inactive ones (4*f*) of 64 Gd in period 6. Chemical evidence, however, does not distinguish between $5f^76d^17s^2$ and $5f^16d^77s^2$, since it is well known that type 3*d*, 4*d*, and 5*d* electrons are generally also chemically inactive after their subgroups are half filled.

TABLE 1

Electron Configurations and Lowest Terms of "Rare-Earth" Spectra

Atomic No.	Element	Theoretical (a)		Experimental							
				Neutral atoms		Singly ionized		Doubly ionized		Trebly ionized	
		Electrons	Terms	Electrons	Terms	Electrons	Terms	Electrons	Terms	Electrons	Terms
58	Ce	$4f^1\ 5d^1\ 6s^2$	$^3\mathrm{H}^\circ$	$(4f^2\ 6s^2)$	$(^3\mathrm{H})$	$4f^2\ 6s^1$	$^4\mathrm{H}$(b)	$(4f^2)$	$(^3\mathrm{H})$(c)	$4f^1$	$^2\mathrm{F}$(d)
59	Pr	$4f^2\ 5d^1\ 6s^2$	$^4\mathrm{K}$	$(4f^3\ 6s^2)$	$(^4\mathrm{I}^\circ)$	$4f^3\ 6s^1$	$^5\mathrm{I}^\circ$(e)				
60	Nd	$4f^3\ 5d^1\ 6s^2$	$^5\mathrm{L}^\circ$	$4f^4\ 6s^2$	$^5\mathrm{I}$(f)	$4f^4\ 6s^1$	$^6\mathrm{I}$(g)				
61		$4f^4\ 5d^1\ 6s^2$	$^6\mathrm{L}$	$(4f^5\ 6s^2)$	$(^6\mathrm{H}^\circ)$						
62	Sm	$4f^5\ 5d^1\ 6s^2$	$^7\mathrm{K}^\circ$	$4f^6\ 6s^2$	$^7\mathrm{F}$(h)	$4f^6\ 6s^1$	$^8\mathrm{F}$(i)				
63	Eu	$4f^6\ 5d^1\ 6s^2$	$^8\mathrm{H}$	$4f^7\ 6s^2$	$^8\mathrm{S}^\circ$(j)	$4f^7\ 6s^1$	$^9\mathrm{S}^\circ$(k)	$4f^7$	$^8\mathrm{S}^\circ$(k)		
64	Gd	$4f^7\ 5d^1\ 6s^2$	$^9\mathrm{D}^\circ$	$4f^7\ 5d^1\ 6s^2$	$^9\mathrm{D}^\circ$(l)	$4f^7\ 5d^1\ 6s^1$	$^{10}\mathrm{D}^\circ$(m)				
65	Tb	$4f^8\ 5d^1\ 6s^2$	$^8\mathrm{H}$	$(4f^9\ 6s^2)$	$(^6\mathrm{H}^\circ)$						
66	Dy	$4f^9\ 5d^1\ 6s^2$	$^7\mathrm{K}^\circ$	$(4f^{10}\ 6s^2)$	$(^5\mathrm{I})$						
67	Ho	$4f^{10}\ 5d^1\ 6s^2$	$^6\mathrm{L}$	$(4f^{11}\ 6s^2)$	$(^4\mathrm{I}^\circ)$						
68	Er	$4f^{11}\ 5d^1\ 6s^2$	$^5\mathrm{L}^\circ$	$(4f^{12}\ 6s^2)$	$(^3\mathrm{H})$						
69	Tm	$4f^{12}\ 5d^1\ 6s^2$	$^4\mathrm{K}$	$4f^{13}\ 6s^2$	$^2\mathrm{F}^\circ$(n)	$4f^{13}\ 6s^1$	$^3\mathrm{F}^\circ$(n)				
70	Yb	$4f^{13}\ 5d^1\ 6s^2$	$^3\mathrm{H}^\circ$	$4f^{14}\ 6s^2$	$^1\mathrm{S}$(o)	$4f^{14}\ 6s^1$	$^2\mathrm{S}$(o)				
71	Lu	$4f^{14}\ 5d^1\ 6s^2$	$^2\mathrm{D}$	$4f^{14}\ 5d^1\ 6s^2$	$^2\mathrm{D}$(p)	$4f^{14}\ 6s^2$	$^1\mathrm{S}$(p)	$4f^{14}\ 6s$	$^2\mathrm{S}$(p)		
90	Th	$6d^2\ 7s^2$	$^3\mathrm{F}$	$6d^2\ 7s^2$	$^3\mathrm{F}$(q)	$6d^2\ 7s^1$	$^4\mathrm{F}$(r)	$6d^2$	$^3\mathrm{F}$(s)	$6d^1$	$^2\mathrm{D}$(t)
91	Pa	$6d^3\ 7s^2$	$^4\mathrm{F}$	$(5f^2\ 6d^1\ 7s^2)$	$(^4\mathrm{K})$	$(5f^2\ 7s^2)$	$(^3\mathrm{H})$				
92	U	$6d^5\ 7s^1$	$^7\mathrm{S}$	$5f^3\ 6d^1\ 7s^2$	$^5\mathrm{L}^\circ$(u)	$5f^3\ 7s^2$	$^4\mathrm{I}^\circ$(f)				
93	Np			$(5f^4\ 6d^1\ 7s^2)$	$(^6\mathrm{M})$	$(5f^4\ 7s^2)$	$(^5\mathrm{I})$				
94	Pu			$(5f^5\ 6d^1\ 7s^2)$	$(^7\mathrm{K}^\circ)$	$(5f^5\ 7s^2)$	$(^6\mathrm{H}^\circ)$				
95	Am			$(5f^6\ 6d^1\ 7s^2)$	$(^8\mathrm{H})$	$(5f^6\ 7s^2)$	$(^7\mathrm{F})$				
96	Cm			$(5f^7\ 6d^1\ 7s^2)$	$(^9\mathrm{D}^\circ)$	$5f^7\ 7s^2$	$(^8\mathrm{S}^\circ)$				

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Spectroscopic evidence for distinguishing *d*- and *f*-type electrons is unique and unambiguous. There are two kinds of spectroscopic evidence: (1) absorption spectra of compounds in solution and (2) emission spectra of atoms or ions. The absorption spectra of certain compounds in solution are characterized by relatively narrow bands approaching in sharpness atomic spectrum lines. Such absorption bands have been reported for the elements 58 (cerium) to 70 (ytterbium), inclusive, and for 92 (uranium) but not for 21 (scandium), 39 (yttrium), 57 (lanthanum), or 90 (thorium). They have not been reported for transuranic elements, probably because such information is at present secret. It is assumed that these bands are associated with the presence of *f*-type electrons in these ions, but this evidence is inconclusive as to the exact nature or number of the electrons involved.

The only way to distinguish the different types of electron orbits and to determine how many of each are present in an atom or ion is by way of the characteristic emission spectrum. Experimental analyses of spectral structures, supported in most cases by the Zeeman effect, have revealed the true electronic structure of atoms. Being, in general, extremely complex, the spectra of rare earths have been the last to succumb to structural analysis. Some are only partially analyzed, and others are still untouched, but sufficient information is now at hand to justify its review in connection with the question under discussion. The results are summarized in Table 1, where small letters in parentheses (a, b, c, etc.) refer to publications cited in the table and other symbols in parentheses represent extrapolations or predictions based on the analyses of neighboring spectra. The extrapolations are made on the assumption that for the production of successive ions and spectra the principal ionization always occurs by removal of the least firmly bound electron without any change or redistribution of the remaining electrons. Thus, if the normal configuration of Ce II is $4f^26s^1$, it is predicted that the normal configuration of Ce I will be $4f^26s^2$, and not $4f^15d^16s^2$. This is not a universal rule, since, for example, the normal configurations of La I and La II are found to be $5d^16s^2$, and $5d^2$, respectively, but it is valid for all rare-earth spectra that have been analyzed.

In 1932 Russell and Meggers (*4*) identified in La I and La II spectra excited states due to configurations involving $4f$ electrons, called attention to the fact that the terms produced by the $4f$ electrons lie lower than those arising from the $6p$ electron, and stated that this is obviously related to the fact that $4f$ electrons are bound into the normal state of the directly following elements, 58 (cerium) to 71 (lutecium), while the $6p$ electrons begin to be similarly bound only in element 81 (thallium). If my prediction for Ce is correct, the normal configuration of $5d^16s^2$ for 57 La becomes $4f^26s^2$ for 58 Ce.

Long ago the spectral analyses of 4th period elements containing $3d$ electrons revealed that an extra electron is seized by the 4th atom (24, chromium) to half fill the group and again by the 9th (29, copper) to fill it completely. Spectral analyses of 5th-period elements also proved that in atomic accretion an extra $4d$ electron is seized by the 3rd (41, columbium) and following atoms and again by the 8th (46, palladium). In the 6th period a similar tendency prematurely to half fill or wholly fill the $4f$ shell was expected, but it was not known where these accelerated accessions would begin. Spectroscopic results now available indicate that an extra $4f$ electron most likely is acquired at the very beginning (58, Ce) and again immediately after the shell is half filled (65, terbium). The $4f$ subgroup is half filled in the 6th rare earth (63, europium) and completely filled in the 13th (70, ytterbium). These facts explain the occasional divalent character of 63 Eu and 70 Yb atoms and suggest that the common compounds in which all rare earths are trivalent involve excited states ($5d^16s^2$ or $5d^26s^1$) rather than ground states (except 64 Gd and 71 Lu).

The facts concerning $5f$ electrons in the 7th period appear to be somewhat different. According to present spectroscopic information no *f*-type electrons are present in the normal states of 90 Th atoms or ions. The normal state of Th IV is ascribed to $6d^1$, that of Th III to $6d^2$ (probably), that of Th II to $6d^27s^1$, and that of Th I to $6d^27s^2$ (probably). The best-analyzed spectrum of this group is Th II, in which excited states identified with $5f$ electrons begin 4,490 cm.$^{-1}$ above the ground level, thus anticipating the binding of such electrons in the normal structures of succeeding atoms. It appears very likely that two $5f$ electrons will be found in the normal configuration of element 91 (protoactinium), because reliable analyses of the first two spectra of 92 U have proved conclusively that these atoms and ions contain three $5f$ electrons as a minimum. The ground state of U II is $5f^3$-$7s^2$. Levels arising from $5f^36d^17s^1$ begin at 289 cm.$^{-1}$, and those arising from $5f^36d^2$ begin at 4,585 cm.$^{-1}$ Other energy levels found in the U II spectrum have been identified with the electron configurations $5f^47s^1$, and $5f^5$. The ground state of U I is $5f^36d^17s^2$, and levels from $5f^36d^27s^1$ begin at 6,249 cm.$^{-1}$ This spectroscopic answer to the $5f$ question is positive and decisive; it was made available to the Manhattan Project on February 7, 1944, and was released to the public by Kiess, Humphreys, and Laun (*1*) on March 9, 1946. The preferred oxidation state VI of 92 U is interpreted to mean that in this case three $5f$, one (or two) $6d$, and two (or one) $6s$ electrons contribute equally to valence bonds, and the gradual shift in preferred oxidation state to III with higher atomic numbers is simply explained by the increase in stability of the $5f$ group as this shell approaches a condition of being half filled, at which point it no longer participates in the formation of chemical compounds. Although the electron configurations of transuranic elements are predicted with considerable confidence, any opportunities for testing the predictions by direct spectroscopic observation and interpretation should not be neglected.

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