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Title: The Discovery of Plutonium Reorganized the Periodic Table
and Aided the Discovery of new Elements.

Author(s): David L. Clark

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The Discovery of Plutonium Reorganized the Periodic Table and Aided the Discovery of new Elements.

David L. Clark, Los Alamos National Laboratory, 2009

The Periodic Table

The modern Periodic Table derives principally from the work of the great Russian scientist Dimitri Mendeleev, who in 1869 enunciated a “periodic law” that the properties of the elements are a periodic function of their atomic weights, and arranged the 65 known elements in a “periodic table”. Fundamentally, every column in the main body of the Periodic Table is a grouping of elements that display similar chemical and physical behavior. Similar properties are therefore exhibited by elements with widely different mass. Chemical periodicity is central to the study of chemistry, and no other generalization comes close to its ability to systematize and rationalize known chemical facts.

With the development of atomic theory, and an understanding of the electronic structure of atoms, chemical periodicity and the periodic table now find their natural explanation in the electronic structure of atoms. Moving from left to right along any row, the elements are arranged sequentially according to nuclear charge (the atomic number). Electrons counter balance that nuclear charge, hence each successive element has one more electron in its configuration. The electron configuration, or distribution of electrons among atomic orbitals, may be determined by application of the Pauli principle (paired spin in the same orbital) and the aufbau principle (which outlines the order of filling of electrons into shells of orbitals – s, p, d, f, etc.) such that in a given atom, no two electrons may have all four quantum numbers identical.

The Actinide Concept

In 1939, only three elements were known to be heavier than actinium: thorium, protactinium, and uranium. All three exhibited variable oxidation states and a complex chemistry. Thorium, protactinium and uranium were assumed to be d-transition metals and were placed in the Periodic Table under hafnium, tantalum, and tungsten, respectively. By 1940, McMillan and Abelson bombarded uranium atoms with slow neutrons and successfully identified atoms of element 93, which they named neptunium after the planet Neptune. This rapidly set the stage for the discovery of the next succeeding element, plutonium (Seaborg, McMillan, Kennedy, and

Wahl, 1940), named after the next planet away from the Sun, Pluto. The newly discovered elements were presumed to fit comfortably in the Periodic Table under rhenium and osmium, respectively, as seen in Figure 1.

Periodic Table of the Elements - 1941

1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Th	Pa	U	Np	Pu										

* Lanthanides

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
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Figure 1. The Periodic Table in 1941 placed actinide elements Th - Pu (shown in red) in an incorrect position under the 5d elements Hf - Os (shown in yellow).

However, subsequent tracer chemical experiments showed that neptunium and plutonium were closer in their chemical properties to uranium than their presumed homologues, rhenium and osmium. Spectroscopic evidence also indicated that the new elements were not typical d-transition elements, but had f-electrons in their valence shell. Thus, several researchers, including McMillan and Wahl, and Zachariasen at Los Alamos, suggested that these elements might be part of a second inner-transition series in which the 5f-electron subshell was being filled. It was not clear, however, where the new series would begin*. [*McMillan had proposed a “uraninide series” that started with neptunium, but attempts to isolate elements with atomic numbers 95 and 96 based on assumed similarities to uranium were unsuccessful. Both Wahl and Zachariasen had proposed a thoride series that started with protactinium.]

In 1944, Seaborg proposed that the series started with thorium, and that all of the elements heavier than actinium constituted an “actinide” series similar to the lanthanides. (See Figure 2.) Because the 5f-shell began filling in the same relative position as the 4f-shell, the electronic configuration of elements in the two series would be similar. Guided by the hypothesis that elements 95 and 96 were homologues of europium and gadolinium, new experiments were designed and the elements were uniquely synthesized and separated from all others. The new elements were subsequently named americium and curium.

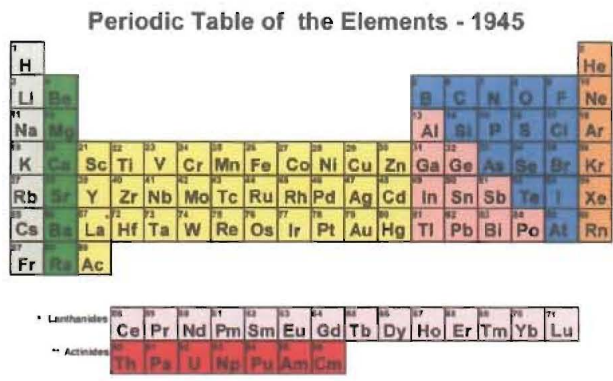


Figure 2. The Periodic Table in 1945 placed actinide elements Th - Cm (shown in red) in their correct positions under the 4f elements, and at the same time introduced the now famous Actinide Concept.

Seaborg's "Actinide Concept" thus played a major role in the discovery of the transplutonium elements. It provided the framework that supported synthesis, isolation, and identification of the succeeding actinide elements berkelium through lawrencium and beyond to the element with Atomic Number 118! But as research has progressed in the study of the actinide elements, it has become clear that the 5f series has a unique chemistry that is distinct from the lanthanides. One of the focal points of study in actinide research has been to better define the scope and limitations of the actinide concept.

The Actinide Elements

Plutonium is one of the actinides, those fourteen elements with atomic numbers 90 to 103 that follow actinium in the Periodic Table (Figure 1a). The figure caption also provides some background material on chemical periodicity and electronic structure. The actinide elements occupy their unique position at the bottom of the Periodic Table and they all contain 5f electrons in their valence shell. Since the valence electrons are the ones that ultimately dictate chemical behavior, we would expect the actinides to behave chemically similar to the only other elements that have f electrons in their valence shell, namely the lanthanides. Those are the fourteen elements with atomic numbers 58 through 71 that are directly above the actinides in the Periodic Table and that have 4f valence electrons.

Chemically, the lanthanides are characterized by relatively homogeneous behavior (especially in aqueous solution). All members tend to be trivalent ions and form similar chemical compounds. In general, the chemical and physical differences between adjacent elements in the series are small. If placed in the main body of the Periodic Table (which is organized according to similarities in chemical traits), all fourteen would occupy the single position set aside for the element lanthanum (number 58). To a large degree, the actinides exhibit this same tendency towards homogeneous chemical behavior. The chemistry of plutonium, for example, is similar to the chemistry of uranium and neptunium. Lanthanide-like behavior, in fact, was the main premise of Glenn Seaborg's "Actinide Concept." Seaborg asserted that the $5f$ subshell begins to fill after actinium, so that the electron configurations of the actinides and lanthanides should be completely analogous, and the two series should behave in a chemically homologous manner.

The $5f$ orbitals are very close in energy to the $6d$'s. In the early part of the actinide series, electrons find it relatively easy to switch between $5f$ and $6d$ configurations, and some of the light actinides exhibit traits that are reminiscent of elements that have at least one unpaired d electron in their valence shell—namely the transition elements.

The transition elements, also called the transition metals, occupy the entire central portion of the Periodic Table (columns 3 through 11). They are the classical hard metals, such as iron, titanium, or tungsten. Many transition elements display a relatively complex chemical behavior that arises because their valence d orbitals extend out to the boundary of the atoms or ions. Electrons in those orbitals are relatively exposed, more accessible for chemical bonding, and are influenced greatly by the surrounding chemical environment. Chemical properties vary significantly between adjacent elements, since the specific chemistry of a transition element is tied strongly to the number of d electrons in its valence shell.

The "light" actinides—from actinium through americium—show some transition metal-like behavior. They exhibit higher oxidation states (up to oxidation state VII) and as a subgroup display more chemical variety than the more lanthanide-like "heavy" actinides from curium through lawrencium. This behavioral split between light and heavy actinides is also evident in the solid state properties of the series.

The division between lighter and heavier actinides is further evident in the electronic configurations of the individual members of the series. As seen in Table 1, the ground state (or

lowest energy) configuration of the thorium atom is $6d^2 7s^2$, indicating that the $6d$ orbital is actually lower in energy than the $5f$ orbital in the ground state neutral atom. As one progresses through the series, the orbital energies invert, with the $5f$'s becoming lower in energy than the $6d$'s, and the gap between the $5f$ and $6d$ orbitals begins to widen. It is still energetically favorable to keep an electron in a d orbital, however, so that the configurations of protactinium through neptunium are all $5f^n 6d^1 7s^2$ ($n=2$ to 4). The presence of the d electron and the competition between the $5f^n 7s^2$ and $5f^{n-1} 6d^1 7s^2$ electronic configurations means that the light actinides tend to supply more bonding electrons in chemical reactions and thus exhibit a more complex chemistry akin to that seen for transition elements.

Table 1. Valence Electron Configurations of Lanthanides and Actinides

lanthanides	symbol	configuration ^a	actinides	symbol	configuration ^b
lanthanum	La	$5d^1 6s^2$	actinium	Ac	$6d^1 7s^2$
cerium	Ce	$4f^1 5d^1 6s^2$	thorium	Th	$6d^2 7s^2$
praseodymium	Pr	$4f^3 6s^2$	protactinium	Pa	$5f^2 6d^1 7s^2$
neodymium	Nd	$4f^4 6s^2$	uranium	U	$5f^3 6d^1 7s^2$
promethium	Pm	$4f^5 6s^2$	neptunium	Np	$5f^4 6d^1 7s^2$
samarium	Sm	$4f^6 6s^2$	plutonium	Pu	$5f^6 7s^2$
europium	Eu	$4f^7 6s^2$	americium	Am	$5f^7 7s^2$
gadolinium	Gd	$4f^7 5d^1 6s^2$	curium	Cm	$5f^7 6d^1 7s^2$
terbium	Tb	$4f^9 6s^2$	berkelium	Bk	$5f^9 7s^2$
dysprosium	Dy	$4f^{10} 6s^2$	californium	Cf	$5f^{10} 7s^2$
holmium	Ho	$4f^{11} 6s^2$	einsteinium	Es	$5f^{11} 7s^2$
erbium	Er	$4f^{12} 6s^2$	fermium	Fm	$5f^{12} 7s^2$
thulium	Tm	$4f^{13} 6s^2$	mendelevium	Md	$5f^{13} 7s^2$
ytterbium	Yb	$4f^{14} 6s^2$	nobelium	No	$5f^{14} 7s^2$
lutetium	Lu	$4f^{14} 5d^1 6s^2$	lawrencium	Lr	$5f^{14} 6d^1 7s^2$

a) outside of the closed [Xe] core

b) outside of the closed [Rn] core

In the latter part of the actinide series, the ground state configuration stabilizes* to $5f^n 7s^2$, where $n = 6$ to 14 , which is completely analogous to the standard $4f^n 6s^2$ configuration of the lanthanides. And like the lanthanides, the $7s$ and empty $6d$ orbitals dominate the chemistry of the heavy actinides resulting in fewer oxidation states and simpler behavior. The reason for the

differences in the light actinide elements relative to the light lanthanide elements has to do with the greater radial extension of $5f$ orbitals compared to $4f$ orbitals, and with relativistic effects that are increasingly important for heavy elements.

The Periodic Table Today

Seaborg's actinide concept of heavy element electronic structure, prediction that the actinides form a transition series analogous to the rare earth series of lanthanide elements, is now well accepted in the scientific community and included in all standard configurations of the Periodic Table. Seaborg's subsequent elaborations of the actinide concept theorized a series of superheavy elements in a transactinide series comprising elements 104 through 121, and a superactinide series inclusive of elements 122 through 153. The discovery of plutonium and development of the actinide concept has allowed for the discovery of an additional 24 elements. In 2009, nearly all of the transactinide elements have in fact been discovered up to element 118. Element 106 was named Seaborgium in honor of Glenn Seaborg.

Periodic Table of the Elements - 2009

1 H																	18 He														
3 Li	4 Be											7 N	8 O	9 F	10 Ne																
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar														
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr														
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe														
55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
		* Lanthanides																													
		** Actinides																													

Figure 3. The Periodic Table in 2009 shows the actinide elements Th - Cm, and the transactinide elements Rf – element 118.