THE CHEMISTRY OF ELEMENTS 93, 94, 95 AND 96 (NEPTUNIUM, PLUTONIUM, AMERICIUM AND CURIUM)

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Four new elements have been added to the list of 92 elements in the last six years. All of these were made artificially; one of them, plutonium (Pu^{239}) has since been discovered in uranium-bearing ore at a concentration of about 1 part in 10^{14}. These elements are known as elements 93, 94, 95 and 96 or as neptunium, (Np), plutonium, (Pu), americium, (Am), and curium, (Cm).

The method of preparation of these elements by means of nuclear transformations together with other facts about them are given in Table I.

Of interest among these isotopes are $_{93}Np^{237}$ and $_{94}Pu^{238}$; these isotopes have long half-lives which make them useful for the determination of many of their chemical properties. Such properties were determined with very minute amounts of these elements by tracer techniques and special micro methods.

Also of interest is $_{94}Pu^{239}$ because of its long half-life and the fact that it captures show neutrons to fission and hence serve as a useful source of atomic energy. $_{93}Np^{239}$ is of interest because it is the intermediate formed in the process of nuclear transmutation of $_{92}U^{238}$ to $_{94}Pu^{239}$.

The first pure compound of an artificially-made element that was ever isolated in weighable quantity was that of plutonium ($_{94}Pu^{239}$) in 1942; now relatively large quantities are available.

NAMES OF THE ELEMENTS

The names of elements 93, 94, 95 and 96 were chosen for the following reasons: Neptunium and plutonium are the elements that appear immediately after uranium and are named for the planets in similar order. Americium ($_{95}Am$) is named for the Americas. It has six 5f electrons and is similar to Europium ($_{63}Eu$) which has six 4f electrons and named for Europe. Curium ($_{96}Cm$) is named after the Curies who did the early work on the radioactive elements. It has seven 5f electrons and is similar to gadolinium ($_{64}Gd$) which has seven 4f electrons and was named after Gadolin who did much of the early work on the rare earths.

CHEMICAL PROPERTIES

Previous to 1940 only a very scant amount of data were available on the chemical properties of the heavy elements. With the discovery of the transuranium elements there was a renewed interest in determining the chemical properties of the heavy elements and their compounds which are employed in the tracer and carrier techniques used in determining properties of extremely small quantities of radioactive material; these properties also aided in the classification of the transuranium elements. Particularly was it necessary to determine the chemistry of plutonium and neptunium very completely because of requirements for separation and purification of $_{94}Pu^{239}$ from the other materials in uranium piles. As a result of this it is now stated that the chemistry of plutonium is as well or

better understood than that of most of the elements in the periodic system. However, most of this information is not yet available for publication.

TABLE I

Isotope	Discovery		How Made	Emits	Half-life
	Date	By Whom			
$_{93}Np^{239}$	1940	McMillan and Abelson	$U^{238} + n \longrightarrow U^{239}$ (23 min) $\downarrow$ $Np^{239} + \beta$	β	2.3 days
$_{93}Np^{237}$	1942	Wahl and Seaborg	$_{92}U^{238} + n \longrightarrow {}_{92}U^{237} + 2n$ (7 days) $\downarrow$ $_{93}Np^{237} + \beta$	α	2.25×10^6 years
$_{94}Pu^{238}$	1940	Seaborg, McMillan, Wahl and Kennedy	$U^{238} + {}_1H^2 \longrightarrow Pu^{238} - 2n$	α	50 years
$_{94}Pu^{239}$ (fissionable)	1941	Seaborg, Segre, Kennedy and Lawrence	$_{93}Np^{239} \longrightarrow {}_{94}Pu^{239} + \beta$	α	24,000 years
$_{95}Am^{241}$	1944	Seaborg, James, Morgan	$_{92}U^{238} + \alpha \longrightarrow {}_{94}Pu^{241} + n$ $\downarrow$ $_{93}Am^{241} + \beta$	α	500 years
$_{95}Am^{242}$			$_{95}Am^{241} + n \longrightarrow {}_{95}Am^{242} + \gamma$	β	18 hours
$_{96}Cm^{242}$	1944	Seaborg, James and Ghiorso	$Pu^{239} + \alpha \longrightarrow {}_{96}Cm^{242} + n$	α	5 months
$_{96}Cm^{242}$			$_{95}Am^{242} \longrightarrow {}_{96}Cm^{242} + \beta$	α	5 months
$_{96}Cm^{240}$			$_{95}Pu^{239} + \alpha \longrightarrow {}_{96}Cm^{240} + 3n$	α	1 month

Legend: n = neutrons.
α = alpha particles.
β = beta particles.
γ = gamma ray.
subscript = atomic number.
superscript = atomic weight.

Neptunium has valence states of 3, 4, 5 and 6. This is somewhat comparable to uranium which has valence states of 3, 4 and 6. Greater oxidizing power is required to oxidize neptunium to its higher state than is required for the higher state of uranium.

Plutonium likewise has valence states of 3, 4, 5 and 6 and still greater oxidizing power is required to convert it to its higher state.

The stability of the valence state of 3 increases from uranium to plutonium and it would be predicted that the maximum stability would probably be obtained with curium (element 96) which has seven 5f electrons.

This prediction is verified by data which now indicate that americium and curium probably exist in aqueous solutions in the oxidation state of 3 only.

Curium is the only one of these four elements that has not been prepared in the form of a pure compound.

All of these new elements are strong alpha particle emitters except Np^{237}; consequently Np^{237} is the only one with which it is relatively safe to work in the laboratory without special precautions to avoid health hazards. Cm^{242} has 10^{14} alpha disintegrations per minute per milligram.

The known properties of these transuranium elements make possible a suggested classification of these elements in terms of a new series similar to the rare earth series. This requires a correction of the older classification of elements 89, 90, 91 and 92 which are actinium, thorium, protactinium and uranium. The meager knowledge of the chemical properties of these four elements (89, 90, 91 and 92) indicated that the 6d electron shell was filling in the following manner.

OLD CLASSIFICATION OF ELECTRON ORBITS

at. no.	Element	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	*6d*	7s
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	*1*	2
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	*2*	2
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	*3*	2
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	*4*	2

If old classification had been correct then the following would be true:

93	Np	(orbits same as above)	*5* 2
94	Pu		*6* 2
95	Am		7 2
96	Cm		*8* 2

This would have made neptunium and plutonium similar to $_{75}Re$ and $_{76}Os$ and to elements 43 and 44 whose electronic configurations are

at. no.	Element	1s	2s	2p	3s	3p	3d	4s	4p	*4d*	4f	5s	5p	*5d*	5f	6s	6p	6d	7s
43	Ma	2	2	6	2	6	10	2	6	*5*		2							
44	Ru	2	2	6	2	6	10	2	6	*6*		2							
75	Re	2	2	6	2	6	10	2	6	10	14	2	6	*5*		2			
76	Os	2	2	6	2	6	10	2	6	10	14	2	6	*6*		2			

But they were found *not* to resemble these elements. This has led Seaborg to suggest that the 5f shell (level) is filling instead of the 6d shell (level). The energy of these two levels is almost the same.[1]

This suggestion leads to the following electronic configuration in which actinium becomes the first member of a new series (similar to the position of lanthanum in the rare earth series). This series then has an electronic configuration similar to the rare earth series and should have like properties.

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[1]See Energy-orbital Chart, in Pauling, "Nature of Chemical Bond," Cornell Univ. Press, 1939, p. 26.

NEW CLASSIFICATION (CALLED ACTINIDE SERIES) OF ELECTRON ORBITS

at. no.	Element	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
89	Ac	filled orbits										2	6	10		2	6	1	2
90	Th											2	6	10	*1*	2	6	1	2
91	Pa											2	6	10	*2*	2	6	1	2
92	U											2	6	10	*3*	2	6	1	2
93	Np											2	6	10	*4*	2	6	1	2
94	Pu											2	6	10	*5*	2	6	1	2
95	Am											2	6	10	*6*	2	6	1	2
96	Cm											2	6	10	*7*	2	6	1	2

These elements can now be compared with the rare earth series which have the following configuration

RARE EARTHS (CALLED LANTHANIDE SERIES)

at. no.	Element	1s	2s	2p	3s	3p	3d	4s	4p	4d	*4f*	5s	5p	5d	5f	6s	6p	6d	7s
57	La	2	2	6	2	6	10	2	6	10		2	6	1		2			
58	Ce	filled orbits						2	6	10	*1*	2	6	1		2			
59	Pr							2	6	10	*2*	2	6	1		2			
60	Nd							2	6	10	*3*	2	6	1		2			
61	Il							2	6	10	*4*	2	6	1		2			
62	Sm							2	6	10	*5*	2	6	1		2			
63	Eu							2	6	10	*6*	2	6	1		2			
64	Gd							2	6	10	*7*	2	6	1		2			
etc.																			

Such a configuration explains satisfactorily the stable valence state of 4 for thorium which compares with a state of 4 for cerium. It also explains the standard valence state of 3 for the rare earths as well as for the actinide series.

It should be noted that the 7s, 6d and 5f energy levels lie so close together that resonance may predominate and determine which level is lowest. Hence the electron configuration may shift from compound to compound.

The question of the difficulty of separation of the transuranium elements may be raised if they have properties similar to those of the rare earths. It is to be noted here that this series has the additional property of radioactivity which makes it possible to affect certain separations on the basis of the difference in the half-life period. This is noticeable with neptunium^{239} (half-life 2.3 days) and plutonium^{239} (half-life 24,000 years).

Addendum: Since writing this paper information has become available on four more new elements, namely, 43, 61, 85, and 87. The report indicates that earlier claims of the discovery of these elements have been disproved and that they exist only as unstable isotopes made by artificial transmutation processes. This completes the list of 96 elements now known. See "Chemical and Engineering News," 25: 431, 1947.

REFERENCES

Seaborg. Chemical and Engineering News, 23, 2190 (1945); *ibid.*, 25, 358 (1947).
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