Title
The Transuranium Elements

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Publication Date
1956-02-17

UCRL-3312

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Contract No. W-7405-eng-48

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February 17, 1956

Preprint of a contribution to Volume 39,
"Handbuch der Physik"

Printed for the U. S. Atomic Energy Commission

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OUTLINE

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A. GENERAL CONSIDERATIONS--THE PLACE OF THE HEAVIEST ELEMENTS IN THE PERIODIC SYSTEM

I. HISTORICAL VIEWS

1. Speculations antedating discovery of transuranium elements. The place of the very heaviest elements in the periodic system is of great scientific interest and is of crucial importance in understanding the physical and chemical properties of these elements. Ideas on this question have varied considerably over the years. Periodic charts have commonly placed thorium, protactinium, and uranium in positions immediately below the elements hafnium, tantalum, and tungsten. The latter group of elements are members of a transition series in which the 5d electron shell is being filled. Hence this earlier placement of the three heavy elements corresponded to the assumption that they are members of a 6d transition series. Indeed thorium, protactinium, and, to a much smaller extent, uranium do show considerable resemblance in chemical properties to the 4d and 5d transition series elements. The electronic configuration beyond the radon core on this basis would be written thus: thorium ($6d^2 7s^2$), protactinium ($6d^3 7s^2$), and uranium ($6d^4 7s^2$).

After the appearance of N. Bohr's classic paper[1] on the quantized nuclear atom many authors suggested that a 5f transition series should start in the vicinity of uranium before completion of the 6d shell. Because the complexity of the theoretical problem made it impossible to calculate exact results and because experimental data were neither plentiful nor definitive there was a wide difference of opinion as to where the new series might be expected to start. Some of these early suggestions were the following: Suguira and Urey[2] predicted that the first entry of the electron into the 5f electron shell should occur at the element with atomic number 95; Bohr[3] chose element 94 as the starting point of the series; Karapetoff[4] and Wu and Goudsmit[5] suggested element 93; Mayer[6] suggested elements protactinium or uranium;

Goldschmidt[7] chose protactinium; Swinne[7a], McLennan, McFay, and Smith[8] and Perrin[9] and Villar[10] suggested thorium.

2. The actinide element concept. The intensive study of the heaviest elements in the last few years including the synthesis and study of transuranium elements up to atomic number 101 has made it certain that, considering the series as a whole, the 5f series of elements begins at actinium in the same sense that the rare-earth series begins with lanthanum. Seaborg has stated the evidence leading to this view in several previous publications.[11-13]

The two series are not strictly comparable, however, because the tripositive state which would be expected to be characteristic of the actinide series does not appear at all in thorium and protactinium and does not become the most stable oxidation state in aqueous solution until americium is reached. For the elements uranium through americium several oxidation states are well established. This is a very real difference from the lanthanide series. It has been interpreted by some as evidence that these lower elements are not members of an actinide series and that they must be members of a 6d transition series. Actually this evidence does not distinguish between the two

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[1] N. Bohr, Phil. Mag. 26, 1, 476 (1913).

[2] Y. Suguira and H. C. Urey, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd., 7, No. 13, 3 (1926).

[3] N. Bohr, Nature 112, 29 (1923).

[4] V. Karapetoff, J. Franklin Inst. 210, 609 (1930).

[5] T. Y. Wu and S. Goudsmit, Phys. Rev. 43, 496 (1933).

[6] M. G. Mayer, Phys. Rev. 60, 184 (1941).

[7] V. M. Goldschmidt, Travaux du Congrès Jubilaire Mendeleev II, 387 (1937).

[7a] R. Swinne, Z. Elektrochem. 31, 417 (1925).

[8] J. C. McLennan, A. B. McFay, and H. G. Smith, Proc. Roy. Soc. (London) A112, 76 (1926).

[9] J. Perrin, "Grains de Matiere et de Lumiere, II-30", Hermannet Cie, Paris (1935).

[10] G. E. Villar, J. Chem. Educ. 19, 329 (1942); Ann. Acad. brasil. scienc. 12, 51 (1940).

series but emphasizes the important fact that the 7s, 6d, and 5f levels lie quite close together in energy in this region.

Additional evidence, particularly magnetic susceptibility data, has established reasonably well that 5f electrons are present in ionic compounds of uranium, neptunium, and plutonium. In the case of protactinium it is not settled whether the electronic configuration beyond the radon core contains 5f electrons and in the case of thorium it seems probable that no 5f electrons are to be expected.

In this connection it is instructive to introduce a figure by Seaborg giving a schematic representation of the comparative electronic binding energy of the 5f and 6d electronic shells for the heaviest elements. This diagram (Figure 1), to which no quantitative significance should be attached, shows the 5f electrons less tightly bound for thorium and lighter elements and progressively more tightly bound for higher elements. In the region near the crossing point the 5f and 6d shells lie so close together that the energy necessary for the shift from one shell to the other may lie within the range of chemical binding energies. This has been pointed out by Seaborg, by Starke[13a] and by others. Thus, for example, the number of 5f electrons found for the gaseous atom may not necessarily be the same as that for the same element in the metallic state, and, in turn, it is possible that neither of these structures would correspond directly to the chemical compounds in which hydration and lattice energies play an important role.

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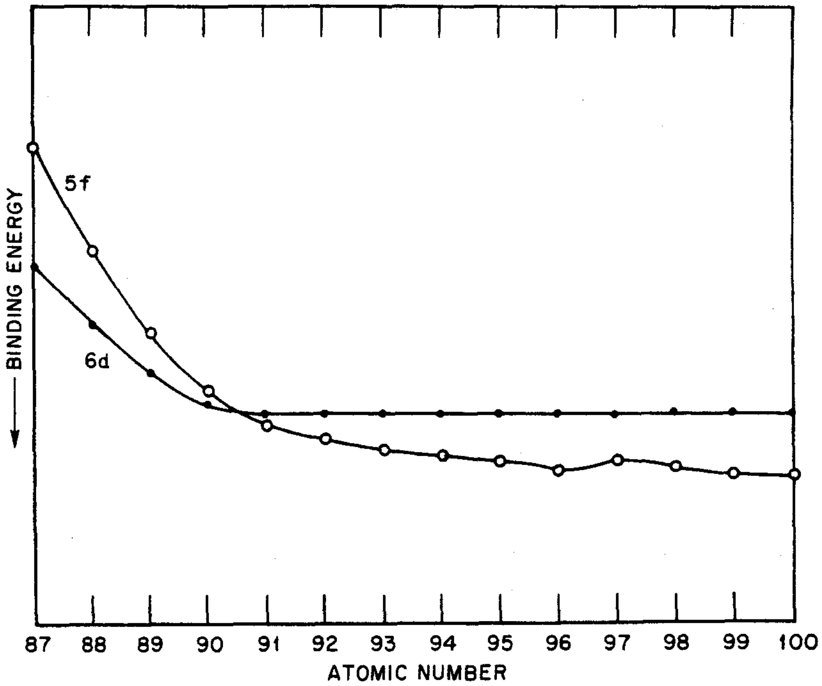
[11] G. T. Seaborg, Paper 21.1 of "The Transuranium Elements", National Nuclear Energy Series, Division IV, Vol. 14B, McGraw-Hill Book Co., Inc., New York, 1949: Hereafter in this text this book will be referred to as N. N. E. S. Vol. 14B "The Transuranium Elements".

[12] G. T. Seaborg, Chap. 17 of "The Actinide Elements", National Nuclear Energy Series, Division IV, Vol. 14A, McGraw-Hill Book Co., Inc., New York, 1954: Hereafter in this text this book will be referred to as N. N. E. S. Vol. 14A "The Actinide Elements".

[13] G. T. Seaborg, Nucleonics 5(5): 16-36 (1949).

[13a] K. Starke, Naturwiss. 34, 69 (1947).

Figure 1. Qualitative representation of electronic binding energies in the heaviest elements.



MU-10957

Figure 1

Seaborg has prepared a list of suggested electronic configurations for the heaviest elements which reflect these considerations of the relative stability of the 5f and 6d electrons and which correspond to spectroscopic data where known. This is shown in Table 1 where additional configurations to complete the series are also included.

Table 1. Suggested electron configurations (beyond radon) for gaseous atoms of actinide elements.

89 - Ac	$6d7s^2$
90 - Th	$6d^27s^2$ (or $5f6d7s^2$)
91 - Pa	$5f^26d7s^2$ (or $5f6d^27s^2$)
92 - U	$5f^36d7s^2$
93 - Np	$5f^57s^2$ (or $5f^46d7s^2$)
94 - Pu	$5f^67s^2$
95 - Am	$5f^77s^2$
96 - Cm	$5f^76d7s^2$
97 - Bk	$5f^97s^2$
98 - Cf	$5f^{10}7s^2$
99 - E	$5f^{11}7s^2$
100 - Fm	$5f^{12}7s^2$
101 - Mv	$5f^{13}7s^2$
102 -	$5f^{14}7s^2$
103	$5f^{14}6d7s^2$

In Section II below the evidence pertaining to the relative significance of 5f and 6d electrons is summarized in some detail. In addition to this principal purpose such a summary is a useful way to present some of the comparative chemistry of the transuranium element group.

II. EVIDENCE RELATING TO THE ACTINIDE CONCEPT

a. Chemical Evidence

3. Tripositive oxidation state in aqueous solution. The characteristic oxidation number of an actinide series as opposed to a thoride series or a uranide series, for example, is III. The earliest member of the series which clearly shows the III state is uranium, the third member. The III state rapidly becomes stabilized in going up the series and is the predominant one for americium and curium (elements 95 and 96), so much so that it is the only oxidation state which is thermodynamically stable in acidic aqueous solution. Berkelium (element 97) has aqueous oxidation states of III and IV analogous to terbium in the rare-earth series whose sesquioxide Tb_2O_3 can be oxidized to TbO_2. The essential point here is that the half-filled shell configuration, $5f^7$ or $4f^7$, is especially stable; berkelium the eighth member of the actinide series strives to reach it by releasing one 5f electron by oxidation; similarly, terbium the eighth member of the lanthanide series achieves the $4f^7$ configuration by conversion to Tb(IV).

The oxidation potentials for the III-IV couple and for the IV-VI couple for the elements of the series show the rapidly increasing stability of the tripositive state in going up the series. These potentials are given in Table 2. Cunningham[14] has presented a figure showing the free energy of formation of the aqueous ions of the actinide elements. From this figure, reproduced here as Figure 2, it is quite clear that the tripositive state becomes stabilized with respect to all other aqueous oxidation states as the atomic number increases.

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[14] B. B. Cunningham Paper P/726, "Peaceful Uses of Atomic Energy, Proceedings of the Geneva Conference", August 1955, United Nations.

Figure 2. Free energies of formation of some aqueous ions of the heavy elements (113.4 k cal mol^{-1} has been added for the ions MO_2^+ and MO_2^{++}) Plot by B. B. Cunningham.[14]

Table 2. Some formal oxidation potentials of the actinide elements in acid solution.

Atomic Number	Element	Potential (Volts)	
		III-IV	IV-VI
92	uranium	+0.6	-0.33
93	neptunium	-0.14	-0.94
94	plutonium	-0.98	-1.04
95	americium	-2.44	-1.34
96	curium	~-3.00(estimated)	
97	berkelium	-1.6	
98 - 101		(no data)	

In the case of curium attempts to effect oxidation of tracer amounts to curium(IV) or to curium(VI) have been uniformly unsuccessful. The 162-day Cm^{242} which has had to be used in most experiments is a difficult isotope for the study of oxidation-reduction equilibria because of the reducing effects of the alpha particles, but additional experiments using the 19-year Cm^{244} gave the same negative results. Tetrapositive curium is known in the solid compound, CmO_2.

All chemical studies of the elements 97 - 101 have been done on a strictly tracer scale. With the exception of berkelium (element 97) the tracer scale behavior in coprecipitation, solvent extraction, and ion exchange is typical of that for the trivalent actinide elements. No evidence is found for oxidation to a higher state except in the case of berkelium where such oxidation is expected.

4. Stability of anhydrous halides. The stability of the solid compounds of the various oxidation states of these elements provides notable evidence for the increased stability of the III state in going up the series. This is best illustrated by a consideration of the solid non-oxygenated halides of these elements. Considering first the fluorides it is noted that no trifluoride appears in thorium or protactinium and that uranium trifluoride can be prepared only under drastic reducing conditions. The trifluorides of neptunium and plutonium can be prepared under relatively mild reducing conditions. For

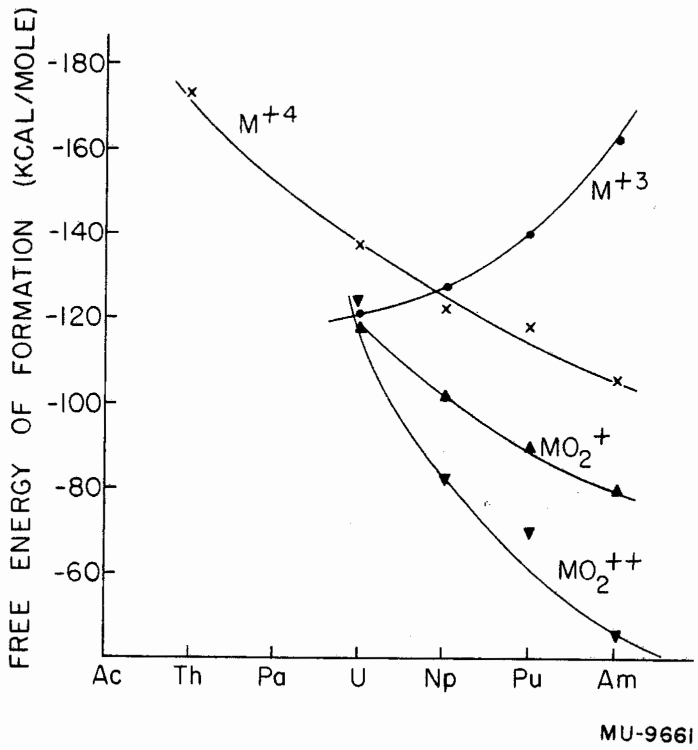
FREE ENERGY OF FORMATION (KCAL/MOLE)
-180
-160
-140
-120
-100
-80
-60
Ac
Th
Pa
U
Np
Pu
Am
M^{+4}
M^{+3}
MO_2^+
MO_2^{++}
MU-9661

Figure 2

the element americium no fluoride higher than the tetrafluoride has been prepared; for curium no fluoride higher than the trifluoride has been prepared.

Shifting now to a consideration of the other halides we note that it has been impossible to prepare any chloride, bromide, or iodide compound of plutonium or americium with an oxidation state higher than III; it has been possible to prepare the chloride and bromide of neptunium in the IV and the III oxidation state in addition to the iodide of oxidation state III but no compounds of these halogens of oxidation number greater than four are known. In the case of uranium a whole series of chlorides are known with oxidation numbers III, IV, V, and VI; the bromides and iodides are known only for the III and IV state.

Table 3 lists all the nonoxygenated halides of the elements from actinium to curium which have been prepared and maintained in the solid state except for the dinalides of thorium. In the case of curium the limitations of working with the 162-day alpha emitter Cm^{242} are such that the table may not be complete, but it seems very doubtful that nonoxygenated halides of curium with an oxidation number greater than III will be prepared.

5. Discussion of evidence on oxidation states. The chemical evidence just discussed indicates that the 5f electrons are more readily removed by oxidation thatn the 4f electrons as should be expected on the basis of the predicted lower ionization potentials of 5f as compared to the potentials of 4f electrons. In a detailed analysis it is necessary to consider the free energy of hydration or of the crystal lattice as well as ionization potentials.

Thus, the tripositive state of thorium cannot exist in aqueous solution. The most stable oxidation state for protactinium is protactinium(V) although there is now rather clear evidence for an easily oxidized protactinium (IV) in aqueous solution.[14a-18] Whether protactinium(III) can be formed remains in doubt. Bouissieres and Haissinsky[17] have reported the reduction of protactinium(IV) to protactinium(IV) in solution by use of amalgamated +inc, chromous chloride, or other strong reducing agents. Fried and Hindman[18] have dissolved anhydrous $PaCl_4$ in an oxygen-free solution of hydrochloric acid and determined its absorption spectrum. This is characterized by three maxima in the ultraviolet region (2760, 2550, and 2237.5 A^o respectively) and by no structure in the visible region. It is of interest that the observed spectrum is remarkably similar

Table 3. Halides of some of the heaviest elements.

Element	Fluorides	Chlorides	Bromides	Iodides
89^{Ac}	AcF_3	ACl_3	$AcBr_3$	AcI_3
90^{Th}	ThF_4	$ThCl_4$ $ThCl_3$	$ThBr_4$ $ThBr_3$	ThI_4 ThI_3
91^{Pa}	PaF_5 PaF_4	$PaCl_5$ $PaCl_4$	$PaBr_5$	PaI_5
92^{U}	Uf_6 UF_5 UF_4 UF_3	UCl_6 UCl_5 UCl_4 UCl_3	UBr_4	UI_4 UI_3
93^{Np}	NfF_6 NpF_5(?)NpF_4 NpF_3	$NpCl_4$ $NpCl_3$	$NpBr_3$	NpI_3
94^{Pu}	PuF_6 PuF_4 PuF_3	$PuCl_3$	$PuBr_3$	PuI_3
95^{Am}	AmF_4 AmF_3	$AmCl_3$	$AmBr_3$	AmI_3
96^{Cm}	CmF_3			

to that of cerium(III) (configuration $4f^1$) since protactinium(IV) might be expected to have the configuration $5f^1$ on the basis of the actinide concept. Fried and Hindman estimate the Pa(IV) - Pa(V) couple to be ∽+0.1 volts.

In the solid state there is definite evidence for lower oxidation states of thorium and protactinium. Thorium triiodide,[19-21] thorium trichloride[22] and thorium tribromide[22] are known as well as the corresponding dihalides.[22] In addition the sesquisulfide[23] and other sulfides of lower oxidation number are known.[20, 23] However, thorium triiodide is not isomorphous with the heavier actinide triiodides and the lower sulfides are semimetallic in character.

In the case of protactinium, Zachariasen[24, 25] and McCullough[26] have obtained crystallographic evidence for the dioxide of protactinium with the fluorite structure. Elson, Fried, Sellers and Zachariasen[25, 27] have prepared $PaCl_4$ and shown it to be isostructural with UCl_4; Zachariasen and Plettinger[28] have identified PaF_4 as isostructural with ThF_4, UF_4, NpF_4, and PuF_4. It seems likely that many other compounds of protactinium(IV) will ultimately be prepared.

It cannot be said whether the electrons in excess of the radon shell are in the 5f or the 6d configuration for these lower oxidation states of

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[14a] G. Bouissières and M. Haissinsky, J. Chem. Soc., 1949 (supplementary issue 2, S54): S256.

[15] R. Elson, Argonne National Laboratory Reports, ANL-4370, Nov. 23, 1949, and ANL-4252, Feb. 17, 1949.

[16] M. Haissinsky and G. Bouissières, Bull. soc. chim. France, 18:146 (1951).

[17] G. Bouissières and M. Haissinsky, Compt. rend 226, 573 (1948); J. Chem. Soc., S. 253:554 (1949).

[18] S. Fried and J. C. Hindman, J. Am. Chem. Soc. 76, 4863 (1954).

[19] E. Hayek and Th. Rehner, Experientia, 5, 114 (1949).

[20] J. S. Anderson and R. W. M. D'Eye, J. Chem. Soc., 1949 (supplementary issue 2, S51): S244.

[21] E. F. Westrum, Jr., private communication, April 1949.

[22] E. Hayek, Th. Rehner, and A. Franck, Monatsh. 82, 575 (1951).

[23] E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, J. Am. Chem. Soc., 72, 4019 (1950).

thorium and protactinium or possibly in some combination of these, since this is the region where the binding energies for the two types of electrons come closest to equality. From the behavior of uranium, neptunium, and plutonium it must be deduced that as many as three of the 5f electrons are given up fairly readily but with increasing difficulty as the atomic number increases.

In the lanthanide series the tripositive state is dominant throughout the series, but, nevertheless, there are several instances of dipositive oxidation states (samarium(II), europium(II), and ytterbium(II)) from which 4f electrons are lost upon oxidation to the corresponding tripositive states. Also the spectroscopic data indicate that in the neutral gaseous atoms there are generally only two electrons (beyond the radon structure) outside the 4f shell although the most important oxidation state is certainly III. Cerium has a well-known tetrapositive oxidation state. Praseodymium, the second lanthanide rare-earth, exhibits a tetrapositive oxidation state. Terbium, as we mentioned above, strives to achieve the half-filled configuration $4f^7$ by oxidation to terbium (IV) although this oxidation has been established only for the anhydrous oxide. This oxidation presumably involves the removal of a 4f electron. These facts indicate that even in the lanthanide series the inner-shell 4f electrons are not bound so tightly that they are quite unavailable for participation in oxidation-reduction reactions. A slight decrease in their binding energy would have resulted in quite different chemical behavior. Or, as Connick[29] has pointed out, if the hydration and lattice free energies of the tripositive ions relative to the ions of other oxidation states were different the III state might not have its pronounced importance.

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[24] W. H. Zachariasen, Report MUC-FWHZ-175, 1946.

[25] R. Elson, S. Fried, P. Sellers, and W. H. Zachariasen, J. Am. Chem. Soc., 72, 5791 (1950).

[26] J. D. McCullough, in Report RL-4.5.56, April 1947.

[27] R. Elson, S. Fried, P. Sellers, Argonne National Laboratory Report ANL-4545, Sept. 1950, p. 9; See also Chap. 5, N.N.E.S. Vol. 14A "The Actinide Elements", 1954.

[28] W. H. Zachariasen and H. A. Plettinger, Argonne National Laboratory Report ANL-4515, Sept. 1950, p. 33.

The known oxidation states of the lanthanide and actinide elements are summarized in Table 4. The similarities of the two series are apparent as are the differences resulting from the more ready oxidation of the actinide group. The uncertain or unusual states are designated with parentheses; possible states with oxidation number less than III are omitted where metallic or possible metallic bonding character is involved.

Table 4. Oxidation states of lanthanide and actinide elements.

Lanthanide elements:															
Atomic number	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Oxidation States						2	2							2	
	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
		4	4						4						
Actinide elements:															
Atomic number	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Element	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	E	Fm	Mv		
Oxidation states															
	$\underline{3}$	(3)	(3)	3	3	3	$\underline{3}$	$\underline{3}$	$\underline{3}$	$\underline{3}$	$\underline{3}$	$\underline{3}$	$\underline{3}$		
		$\underline{4}$	4	4	4	$\underline{4}$	(4)		4						
			$\underline{5}$	5	$\underline{5}$	5	5								
				$\underline{6}$	6	6	6								

Some of the oxidation states shown in Table 4 are observable only under drastic conditions so that their inclusion here may be misleading. On the other hand to list only those states which are stable in aqueous solution also has short-comings since the existence of an aqueous ion, besides being limited by the ionization potentials of the electrons, is affected by the specific chemical processes of hydration and complex formation and is arbitrarily confined within the limits of its oxidation and reduction by water. The most stable oxidation states of the actinide elements are underlined in Table 4

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[29] R. E. Connick, J. Chem. Soc. (Supplementary issue 2, S49): S235.

to show the variation in their stability in going across the series.

6. Crystallographic data - isostructural series. Table 5 shows the crystallographic radii of the tripositive and tetrapositive ions of the actinide elements. The radii of the tripositive lanthanide ions are shown for comparison. As the number of electrons in the f shell increases there is a regular contraction of the ionic radius in both series; in the rare-earth series this is referred to as the "lanthanide contraction". The extensive studies of Zachariasen and his co-workers[30, 31] on the crystal structure of the heavy element compounds have shown a large number of isostructural series of compounds. The facts are summarized in Table 6.

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[30] W. H. Zachariasen, Phys. Rev. 73, 1104 (1948); Numerous papers in Acta Cryst. 1948-1955; J. Chem. Phys. 16, 254 (1948).

[31] W. H. Zachariasen, Chap. 18, N N.E.S. Vol. 14A "The Actinide Elements", 1954.

The large number of isostructural series and the closely-similar and regularly varying crystal radii indicate a smooth transition in going up the series, a transition most easily explained by the steady filling of an inner shell of electrons.

Table 5. Crystal radii of lanthanide and actinide element ions

	Lanthanide Series[1]		Actinide Series[2]			
Number of 4f or 5f Electrons	Element	Radius	Element	Radius A^{o}	Element	Radius A^{o}
0	La^{+3}	1.061	Ac^{+3}	1.11	Th^{+4}	0.99
1	Ce^{+3}	1.034	(Th^{+3})	(1.08)	Pa^{+4}	0.96
2	Pr^{+3}	1.013	(Pa^{+3})	(1.05)	U^{+4}	0.93
3	Nd^{+3}	0.995	U^{+3}	1.03	Np^{+4}	0.92
4	Pm^{+3}	0.979	Np^{+3}	1.01	Pu^{+4}	0.90
5	Sm^{+3}	0.964	Pu^{+3}	1.00	Am^{+4}	0.89
6	Eu^{+3}	0.950	Am^{+3}	0.99		
7	Gd^{+3}	0.938				
8	Tb^{+3}	0.923				
9	Dy^{+3}	0.908				
10	Er^{+3}	0.894				
11	Ho^{+3}	0.881				
12	Tm^{+3}	0.869				
13	Yb^{+3}	0.858				
14	Lu^{+3}	0.848				

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[1] D. H. Templeton and C. H. Dauben, J. Am. Chem. Soc. <u>76</u>, 5237 (1954).

[2] W. H. Zachariasen, Chap. 18 N. N. E. S., Vol. 14A "The Actinide Elements", 1954.

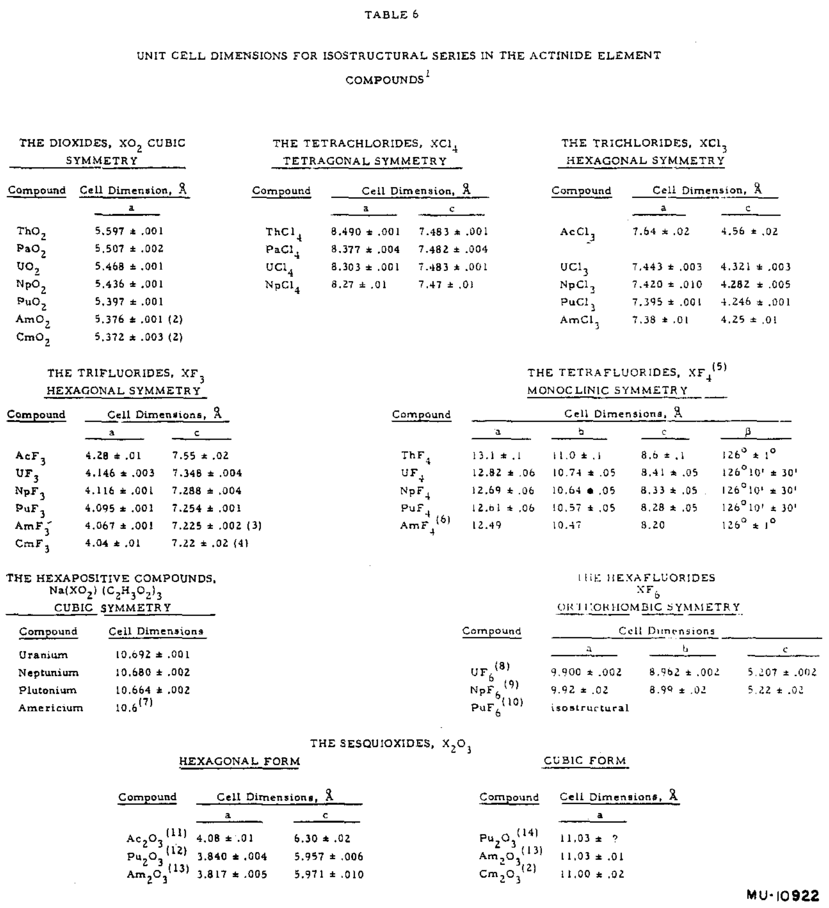

TABLE 6

UNIT CELL DIMENSIONS FOR ISOSTRUCTURAL SERIES IN THE ACTINIDE ELEMENT COMPOUNDS[1]

THE DIOXIDES, XO_2 CUBIC SYMMETRY

Compound	Cell Dimension, Å
	a
ThO_2	5.597 ± .001
PaO_2	5.507 ± .002
UO_2	5.468 ± .001
NpO_2	5.436 ± .001
PuO_2	5.397 ± .001
AmO_2	5.376 ± .001 (2)
CmO_2	5.372 ± .003 (2)

THE TETRACHLORIDES, XCl_4 TETRAGONAL SYMMETRY

Compound	Cell Dimension, Å	
	a	c
$ThCl_4$	8.490 ± .001	7.483 ± .001
$PaCl_4$	8.377 ± .004	7.482 ± .004
UCl_4	8.303 ± .001	7.483 ± .001
$NpCl_4$	8.27 ± .01	7.47 ± .01

THE TRICHLORIDES, XCl_3 HEXAGONAL SYMMETRY

Compound	Cell Dimension, Å	
	a	c
$AcCl_3$	7.64 ± .02	4.56 ± .02
UCl_3	7.443 ± .003	4.321 ± .003
$NpCl_3$	7.420 ± .010	4.282 ± .005
$PuCl_3$	7.395 ± .001	4.246 ± .001
$AmCl_3$	7.38 ± .01	4.25 ± .01

THE TRIFLUORIDES, XF_3 HEXAGONAL SYMMETRY

Compound	Cell Dimensions, Å	
	a	c
AcF_3	4.28 ± .01	7.55 ± .02
UF_3	4.146 ± .003	7.348 ± .004
NpF_3	4.116 ± .001	7.288 ± .004
PuF_3	4.095 ± .001	7.254 ± .001
AmF_3	4.067 ± .001	7.225 ± .002 (3)
CmF_3	4.04 ± .01	7.22 ± .02 (4)

THE TETRAFLUORIDES, XF_4(5) MONOCLINIC SYMMETRY

Compound	Cell Dimensions, Å			
	a	b	c	β
ThF_4	13.1 ± .1	11.0 ± .1	8.6 ± .1	126° ± 1°
UF_4	12.82 ± .06	10.74 ± .05	8.41 ± .05	126°10' ± 30'
NpF_4	12.69 ± .06	10.64 ± .05	8.33 ± .05	126°10' ± 30'
PuF_4	12.61 ± .06	10.57 ± .05	8.28 ± .05	126°10' ± 30'
AmF_4(6)	12.49	10.47	8.20	126° ± 1°

THE HEXAPOSITIVE COMPOUNDS, $Na(XO_2)(C_2H_3O_2)_3$ CUBIC SYMMETRY

Compound	Cell Dimensions
Uranium	10.692 ± .001
Neptunium	10.680 ± .002
Plutonium	10.664 ± .002
Americium	10.6(7)

THE HEXAFLUORIDES XF_6 ORTHORHOMBIC SYMMETRY

Compound	Cell Dimensions		
	a	b	c
UF_6(8)	9.900 ± .002	8.962 ± .002	5.207 ± .002
NpF_6(9)	9.92 ± .02	8.99 ± .02	5.22 ± .02
PuF_6(10)	isostructural		

THE SESQUIOXIDES, X_2O_3

HEXAGONAL FORM

Compound	Cell Dimensions, Å	
	a	c
Ac_2O_3(11)	4.08 ± .01	6.30 ± .02
Pu_2O_3(12)	3.840 ± .004	5.957 ± .006
Am_2O_3(13)	3.817 ± .005	5.971 ± .010

CUBIC FORM

Compound	Cell Dimensions, Å
	a
Pu_2O_3(14)	11.03 ± ?
Am_2O_3(13)	11.03 ± .01
Cm_2O_3(2)	11.00 ± .02

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THE TRI BROMIDES,[15] XBr_3

HEXAGONAL FORM - UCl_3 TYPE

Compound	Cell Dimensions, Å	
	a	c
$AcBr_3$	8.08 ± .04	4.69 ± .02
UBr_3	7.942 ± .002	4.441 ± .002
$\alpha NpBr_3$	7.933 ± .005	4.391 ± .005

ORTHORHOMBIC - $PuBr_3$ TYPE

Compound	Cell Dimensions, Å		
	a	b	c
$\beta NpBr_3$	12.67 ± .05	4.12 ± .03	9.17 ± .04
$PuBr_3$	12.64 ± .05	4.10 ± .03	9.15 ± .04
$AmBr_3$	12.6 ± .1	4.11 ± .04	9.12 ± .05

THE TRI IODIDES,[15] XI_3

ORTHORHOMBIC - $PuBr_3$ TYPE

Compound	Cell Dimensions, Å		
	a	b	c
UI_3	14.01 ± .06	4.32 ± .03	10.01 ± .05
NpI_3	14.03 ± .06	4.30 ± .03	9.95 ± .05
PuI_3	14.03 ± .06	4.30 ± .03	9.92 ± .05
AmI_3	14.0 ± .1	4.31 ± .05	9.9 ± .1

THE OXYCHLORIDES, XOCl

TETRAGONAL SYMMETRY

Compound	Cell Dimensions, Å	
	a	c
AcOCl(5)	4.25 ± .02	7.08 ± .03
PuOCl(5)	4.012 ± .002	6.782 ± .010
AmOCl(13)	4.00 ± .01	6.78 ± .01

THE OXYBROMIDES, XOBr

Compound	Cell Dimensions, Å	
	a	c
AcOBr(5)	4.28 ± .02	7.41 ± .03
PuOBr(5)	4.022 ± .004	7.571 ± .011

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[1] Unless other wise indicated data are taken from W. H. Zachariasen, Chap. 18 N.N.E.S., Vol. 14A, "The Actinide Elements" 1954.

[2] L. B. Asprey, F. H. Ellinger, S. Fried and W. H. Zachariasen, J. Am. Chem. Soc. 77, 1707 (1955).

[3] D. H. Templeton and C. H. Dauben, J. Am. Chem. Soc. 75, 4560 (1953).

[4] L. B. Asprey and F. H. Ellinger, Atomic Energy Commission Declassified Document, AECD-3627.

[5] W. H. Zachariasen, Acta Cryst. 2, 388 (1949).

[6] L. B. Asprey, J. Am. Chem. Soc. 76, 2019 (1954).

[7] L. B. Asprey, S. E. Stephanson and R. A. Penneman, J. Am. Chem. Soc. 73, 5715 (1951).

[8] J. L. Hoard and J. D. Shoupe, in The Chemistry of Uranium, N.N.E.S., Div. VIII, Vol. 5, p. 439, McGraw-Hill Book Co., Inc., N.Y. 1951.

[9] W. H. Zachariasen, U. S. Atomic Energy Commission Report MDDC-1151.

[10] J. Malm and B. Weinstock Paper, paper P/733, Peaceful Uses of Atomic Energy-Proceedings of the Geneva Conference. United Nations, August 1955.

[11] W. H. Zachariasen, Acta Cryst. 2, 388 (1949).

[12] D. H. Templeton and C. H. Dauben, University of California Radiation Laboratory Report UCRL-1886, July 14, 1952.

[13] D. H. Templeton and C. H. Dauben, J. Am. Chem. Soc. 75, 4560 (1953).

[14] W. H. Zachariasen Report CK-1530.

[15] W. H. Zachariasen, Acta Cryst. 1, 265 (1948).

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7. The metallic state. The metallic state has been prepared for the elements thorium through curium. The properties of this series of metals do not correspond to those of the 5d elements, hafnium (element 72) through platinum (element 78). On the contrary the resemblance of the chemical properties of the heavy element metals to those of the rare-earth element metals is quite close. All are highly electropositive and to about the same degree. One notable resemblance to the lanthanide metals is the low density of americium metal (11.7) relative to its preceding neighbors which is precisely the situation with the metallic state of its homologue europium which has a low density with respect to its preceding neighbors. A comparison with tungsten, rhenium, osmium, and iridium shows no such analogy.

8. Ion-exchange behavior. Striking similarities in the chemical behavior of the aqueous tripositive ions of the lanthanide and actinide elements are found in ion-exchange behavior. The very difficult problem of the separation of the rare-earth fission product elements was solved on the wartime Plutonium Project by adsorbing the aqueous ions on top of a column of cation-exchange resin and then selectively eluting the elements with a complexing agent such as ammonium citrate buffered to a suitable pH.[32] The effect of small differences in complex formation and of small differences in resin adsorbability, both effects presumably influenced by small differences in hydrated ionic radii, are superimposed in this method with the result that neighboring lanthanide elements can be separated from each other.

When the chemical similarities of the tripositive lanthanide and actinide elements became apparent, it was only natural that the ion-exchange method should be applied to the latter. Cunningham, Tompkins, and Asprey[33] first used the ion-exchange method to perform a separation of tripositive americium from curium.

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[32] Symposium on Ion Exchange, J. Am. Chem. Soc. 69, 2769-2881 (1947)

[33] B. B. Cunningham, E. R. Tompkins, and L. B. Asprey, unpublished work (1947).

When the column elution behavior of the two series is compared, the analogy even to details is striking with some eluting agents. Figure 3 shows elution curves for lanthanide and actinide element ions. In both cases the mixture of elements was adsorbed on a short column of Dowex-50 cation exchange resin and eluted selectively with lactic acid buffered to a suitable pH.

Figure 3. Elution of trace concentrations of tripositive actinide elements (upper curve) and tripositive lanthanide elements (lower curve) from Dowex-50 cation exchange resin with ammonium lactate eluting solution. Figure reproduced from S. G. Thompson, *et al*, J. Am. Chem. Soc. 76, 6229 (1954).

A remarkable analogy can be seen in the spacing between the californium - berkelium - curium - americium group and their rare-earth homologues dysprosium - terbium - gadolinium - europium. These spacings reflect the relative changes in ionic radii which presumably determine the relative separations in the ion-exchange adsorption method. It can be concluded, therefore, that the same sequence of changes in the ionic radius is encountered on filling the 5f electron shell as occurs on filling the 4f shell; therefore, it seems clear that curium represents the midpoint in the actinide transition series of elements in view of its position analogous to gadolinium.

b. Physical Evidence

9. Absorption and fluorescence spectra in aqueous solution and crystals. The absorption spectra of aqueous ions of uranium, neptunium, plutonium, and americium show very sharp absorption bands; similarly, adsorption of light in crystal compounds of these elements occurs in very sharp bands. This situation is very reminiscent of the lanthanide series where the absorption is ascribed to electronic transitions involving the 4f electrons. It is believed that the upper and lower states in these transitions belong to the same configuration $4f^n$ and differ only in their electronic coupling to different L or S values.[36, 37] For an ion with only one 4f electron, such as cerium(III) or with thirteen 4f electrons, such as ytterbium(III), no such transitions are expected and none are found. The sharpness of the transition is due to the shielding of the 4f electrons by the 5s and 5p electrons. In the absorption spectra of crystals extra lines due to the Stark effect of the crystal field were observed. The literature in this field is quite extensive, both in experimental studies and theoretical calculations and correlations. Enough is known to be sure of the essential correctness of the interpretation on the basis

of 4f

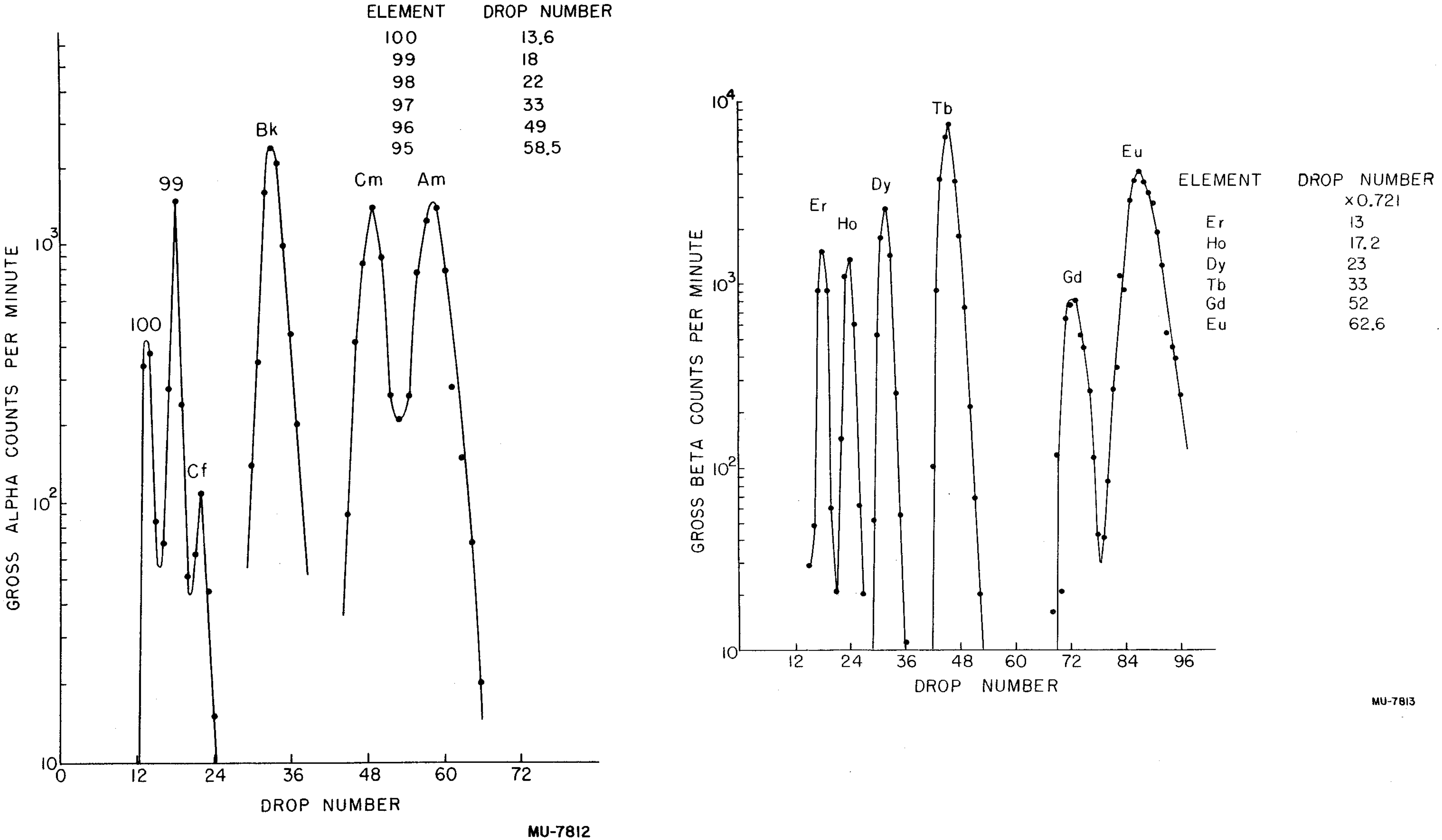
ELEMENT DROP NUMBER
100 13.6
99 18
98 22
97 33
96 49
95 58.5
100
99
Cf
Bk
Cm
Am
GROSS ALPHA COUNTS PER MINUTE
10^3
10^2
10
0
12
24
36
48
60
72
DROP NUMBER
MU-7812
Er
Ho
Dy
Tb
Gd
Eu
ELEMENT DROP NUMBER ×0.721
Er 13
Ho 17.2
Dy 23
Tb 33
Gd 52
Eu 62.6
GROSS BETA COUNTS PER MINUTE
10^4
10^3
10^2
10
12
24
36
48
60
72
84
96
DROP NUMBER
MU-7813

Figure 3

electrons, but many details are not satisfactorily explained. A brief review is given by Yost, Russell, and Garner[38] where references to the pre-1946 literature may be found.

It seems highly likely that the sharp absorption spectra of the actinide elements is due to the presence of 5f electrons. A number of details may be cited in support of this view. In both series the absorption spectra undergo similar simplification as the middle of the two series is approached, that is, as the elements gadolinium and curium, with their seven 4f or 5f electrons, are approached. This may be explained qualitatively as being due to the increased stability of the ground state with respect to the first excited state, leading to energy differences which correspond to absorption in the ultraviolet region. Curium (III) exhibits no apparent absorption in aqueous solution at wave lengths above about 3200 Å. Similarly, gadolinium shows no absorption at wave lengths above about 2800 Å.

The homologous ions americium(III) and europium(III) have analogous absorption peaks at 5000 Å and 4000 Å, respectively, and show striking similarity even in their fine structure. The aqueous-solution absorption spectra of tri-positive uranium, neptunium, and plutonium show many sharp absorption peaks in the visible region. Solutions of these ions are highly colored. Sharp absorption bands undoubtedly involving 5f electrons have also been found in aqueous solution for the other oxidation states of plutonium and neptunium. The absorption spectra of the transuranium elements will be found later in this article under the discussion of the individual elements. Gruen[39] has carefully analyzed the very similar absorption spectra of NpO_2^+ and PuO_2^{++} and has concluded that the $5f^2$ configuration is involved. In the case of neptunium(VI) which contains only one 5f electron no such absorption bands are expected and none are found. Absorption spectra similar to each other are observed for the aqueous ions of the isoelectronic series uranium (IV) - neptunium(V) - plutonium(VI) where the configuration is presumably $5f^2$ and for the isoelectronic series uranium(III)

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[36] S. Freed, Phys. Rev. <u>38</u>, 2122 (1931).

[37] J. H. Van Vleck, J. Phys. Chem. <u>41</u>, 67 (1937).

[38] D. M. Yost, H. Russell, Jr., and C. S. Garner, "The Rare-Earth Elements and Their Compounds", John Wiley and Sons, Inc., New York, 1947.

neptunium(IV) - plutonium(V) where the electron configuration is presumably $5f^3$.[40]

Jørgensen[40a] applied the Condon-Shortley[40b] theory of interaction between a pair of electrons in different coupling schemes to calculate the expected transitions for the $5f^2$ configuration. The calculated values were in good agreement with many of the absorption peaks observed in solutions of uranium (IV). Jørgensen concludes that the configuration must be $5f^2$ beyond the emanation shell; $6d^2$ electrons should show broad band absorption and seem to be ruled out clearly. Jørgensen also discussed systems with three or more f-electrons and compared the theoretical predictions with absorption spectra of various actinide ions in aqueous solution.

Absorption spectra of crystals are somewhat sharper than solution spectra. The absorption spectrum of solid americium trichloride contains sharp lines of the order of 1 to 5 A° wide even when the measurements are made at room temperature.[41] This sharpness ranks with the finest ever observed, and, in fact, only the spectrum of tripositive europium ion is comparable. The absorption spectrum of the latter originates from a ground state $4f^6$ $(^7F_0)$ configuration; it seems likely that the ground state of tripositive americium also contains six 5f electrons. The absorption spectra of crystalline uranium tetrachloride, uranium trichloride, neptunium tetrachloride and plutonium trichloride also have sharp lines suggesting rather strongly that transitions take place between upper and lower states in which the $5f^n$ configuration is preserved.[41, 42]

It has been pointed out[43] that one difference between the absorption spectra of the actinide as compared to the lanthanide ions is that the relative intensity of absorption is much greater for the principal bands of the former than for the equivalent bands in the latter. In the case of the tripositive ions the intensity of absorption is as much as ten times as great for the transuranium elements. The transuranium element ions of higher charge show even more intense absorption, as much as one hundred times as great as for the tripositive lanthanide ions. These observations are in line with many other lines of evidence which suggest that the 5f electrons are much less shielded than 4f electrons and hence are much more readily influenced by the external environment.

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[39] D. M. Gruen, J. Chem. Phys. 20, 1818 (1952).

[40] R. Rohmer, R. Freymann, A. Chevet, and P. Hamon, Bull. Soc. Chem. France, 1952: 603.

[40a] C. K. Jørgensen , Dan. Mat. fys. Medd. 29, (1955) No. 7.

[40b] E. U. Condon and G. H. Shortley, "Theory of Atomic Spectra", Cambridge Press, 1935.

[40c] C. K. Jørgensen, Dan. Mat. fys. Medd 29 (1955) No. 11.

[41] S. Freed and F. J. Leitz, Jr., J. Chem. Phys. 17, 540 (1949).

[42] K. M. Sancier and S. Freed, Brookhaven National Laboratory Report, BNL-1008, 1951.

[43] R. Sjoblom and J. C. Hindman, J. Am. Chem. Soc. 73, 1749 (1951).

Fluorescence is well known in a number of rare-earth ions. This fluorescence is almost certainly due to the presence of 4f electrons although the complexities in interpretation of the details are very great. Fluorescence has been observed by Gruen and co-workers[44] in mixed crystals of americium trichloride and lanthanum trichloride. The fluorescence is weakly self-excited at room temperature due to the radioactivity of Am^{241} and is strongly excited by irradiation with a mercury lamp. Many of the lines correspond exactly with lines found in the absorption spectrum and are interpreted as representing transitions from excited electronic states to the $^7F_0$ level of the ground state multiplet. A comparison of the fluorescence spectrum of americium(III) and its lanthanide homologue, europium(III), shows the difference that transitions from only the two lowest-lying electronic levels above the $^7F_0$ ground state are observed in the americium case whereas transitions from five relatively low-lying excited electronic levels are involved in europium. The wider spacing of the americium levels is in agreement with magnetic susceptibility data to be discussed later.

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[44] D. M. Gruen, J. G. Conway, R. D. McLaughlin, and B. B. Cunningham, unpublished results, January 1956.

Fluorescence has also been observed[44] in mixed crystals of plutonium trichloride and lanthanum trichloride. The fluorescence is weakly self-excited and is brought out strongly upon irradiation with a mercury lamp.

10. Magnetic susceptibility data - theoretical considerations. The presence of unpaired electrons in the heaviest elements should and does lead to paramagnetism. This magnetic behavior is expected whether the unpaired electrons are in the 5f or the 6d shell; quantitative measurements of magnetic susceptibilities of compounds of the heaviest elements should in principle lead to the resultant magnetic moments in units of Bohr magnetons and distinguish between possible electron configurations. The considerable amount of experimental data now available, in general, lends rather strong support to the actinide concept, but quantitative agreement of theory and experiment have not been achieved because of complexities in the situation which make prediction of the magnetic moment from the electron configuration more difficult than in the case of the lanthanide rare-earths. As is the case for other lines of evidence, the situation is not conclusive for the early members of the series. Nevertheless for the elements neptunium and plutonium the magnetic evidence provides some of the strongest evidence for the actinide concept.

The usual approximate approach is to calculate a molar susceptibility from the well-known expression:

$$\chi_m = Ng^2B^2J(J+1)/3kT \tag{10.1}$$

where N = Avogadro's number

$g =$ Lande splitting factor $= 1 + \frac{S(S+1) + J(J+1) - L(L+1)}{2J(J+1)}$

$B =$ Bohr magneton $= eh/2\pi mc$

$J = L + S =$ total angular momentum of atom

$k =$ Boltzmann constant

$T =$ absolute temperature

The value of J is taken from the ground state term value calculated according to Hund's rules.[45] Russell-Saunders coupling is assumed and out of the possible terms allowed by the Pauli principle, Hund supposes that the one of highest multiplicity, i.e. greatest value of $2S + 1$, lies lowest. In those cases where several values of L are possible with the same multiplicity the greatest L consistent with this S is chosen. The minimum possible J lies lowest when the 5f electrons are less than seven in number; the maximum possible J lies lowest when more than seven f-electrons are present. The predicted ground states for the members of the series are: $5f^1(^2F_{5/2})$, $5f^2(^3H_4)$, $5f^3(^4I_{9/2})$, $5f^4(^5I_4)$, $5f^5(^6H_{5/2})$, $5f^6(^7F_0)$, $5f^7(^8S_{7/2})$, $5f^8(^7F_6)$, $5f^9(^6H_{15/2})$, $5f^{10}(^5I_8)$, $5f^{11}(^4I_{15/2})$, $5f^{12}(^3H_6)$, $5f^{13}(^2F_{7/2})$ and $5f^{14}(^1S)$.

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[45] F. Hund, Z. Physik 33, 855 (1925).

The equation 10.1 is, strictly speaking, applicable only to gaseous ions and furthermore, it neglects a small diamagnetic term. All experimental measurements for the heavy elements are made not on gaseous ions but on solutions or crystals. The justification for the use of equation 10.1 is the one applied previously to the rare-earths, namely, that the inner shell of electrons are shielded from the effects of the solution or crystal environment by the s^2 and p^6 electrons in the next shell. This is nearly completely true for the lanthanides; it must be regarded as an approximation for the heavy elements.

It is possible also to calculate theoretically the magnetic susceptibilities expected for unpaired electrons in the 6d shell. In doing this one usually assumes that the orbital contribution to the magnetic moment is quenched by field effects within the crystal or solution or by Heisenberg exchange forces. This leads to a "spin-only" value for the magnetic susceptibility given by the expression:

$$\chi_m = \frac{NB^2}{3kT} \left[4S \left(S + 1 \right) \right] \tag{10.2}$$

where S is the vector sum of the electron spins of the unpaired electrons.

The calculated molal susceptibilities for $6d^n$ electron configurations, where n is 3 or greater, are much too high to agree with experimental measurements on actinide element ions. The calculated values for one, two, and three unpaired 6d electrons are 1245, 3333, and 6250 respectively in c. g. s. units x 10^6. Experimental values for ions with one, two, or three unpaired electrons frequently fall between these values and the ones given by equation 10.1. In such cases the decision between $5f^n$ or $6d^n$ configurations is not simple and requires more detailed experiments and analysis with suitable evaluation of all factors which may contribute to quenching of the orbital contribution of f as well as d electrons. Some of these factors will be mentioned in the following review of the experimental data.

11. Magnetic susceptibility data - experimental studies. Calvin[46] has measured and compared the magnetic susceptibilities of ThS and CeS, analogous compounds which might be expected to possess two magnetic electrons; similarly he measured and compared the magnetic susceptibilities of Th_2S_3 and Ce_2S_3 in which the metallic ion might be expected to possess one magnetic electron. Both cerium compounds are paramagnetic to an amount consistent with the presence of unpaired 4f electrons. The thorium compounds are not paramagnetic. This is most reasonably interpreted as indicating the presence of 6d rather than 5f electrons in thorium. In the sulfides the interatomic distances are so small that the magnetic d electrons on neighboring thorium atoms can pair to form a metallic bond. Dawson and D'Eye[47] have similarly found Th_2Se_3 to be slightly diamagnetic.

Howland and Calvin[48] have measured the magnetic susceptibilities of the cations of uranium, neptunium, plutonium, and americium The results are presented in Figure 4 together with curium data of Crane and Cunningham to be mentioned later.[50] The qualitative similarity of the actinide curve with the lanthanide curve is interpreted as evidence for the $5f^{n}$ electron configuration for the magnetic electrons. The fact that the experimental effective magnetic moments are generally lower than the theoretical values (given in the figure title) is interpreted as resulting from a Stark effect produced by electric fields of anions and of water dipoles. Partial failure of the Russell-Saunders approximation could also account for some of the discrepancy. Crane, Wallman and Cunningham[49] made measurements on solid AmF_3 and obtained for the molar susceptibilities, 1040 ± 300 at 295° K, 1290 ± 300 at 199° K and 1740 ± 300 at 77° K in c.g.s. units x 10^{6}. Graf, Cunningham and co-workers[49a] measured the susceptibility of americium metal and obtained a value of 1000 ± 250 x 10^{-6} c.g.s. units at 300° K.

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[46] M. Calvin as reported in E. D. Eastman et al, J Am. Chem. Soc. 72, 4019 (1950) and 72, 2248 (1950).

[47] J. K. Dawson and R. D'Eye as reported by Dawson, Nucleonics 10, (9) 39 (1952).

[48] J. J. Howland and M. Calvin, J. Chem. Phys. 18, 239 (1950).

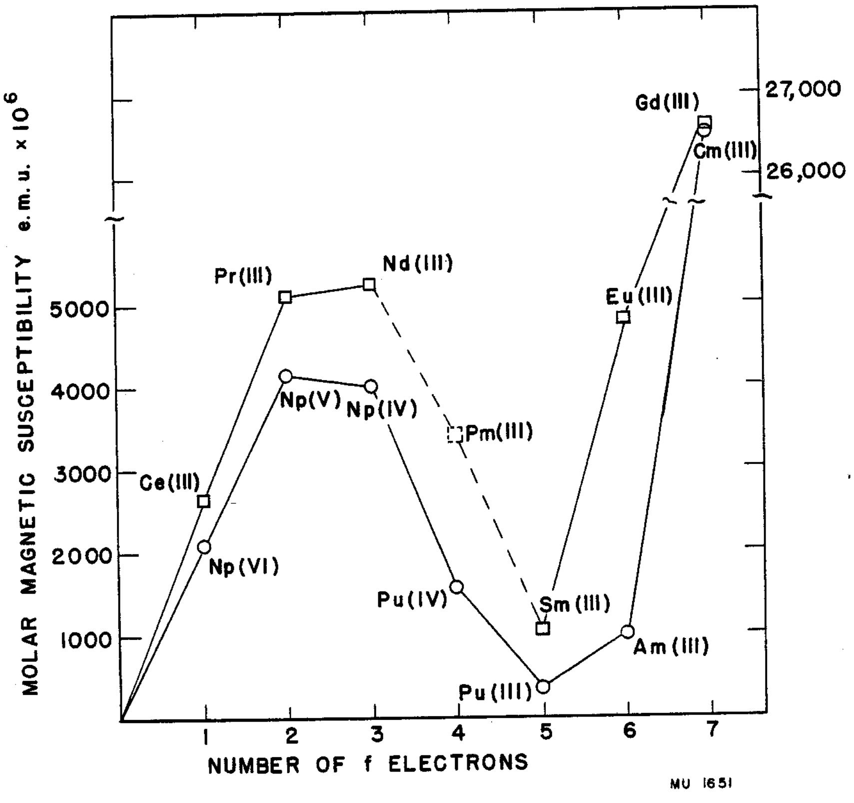
[49] W. W. T. Crane, J. C. Wallmann and B. B. Cunningham, University of California Radiation Laboratory Report, UCRL-846 (1950).

[49a] P. Graf, B. B. Cunningham, et al, University of California Radiation Laboratory Report UCRL-3280; submitted for publication, J. Am. Chem. Soc. (1956).

[50] W. W. T. Crane and B. B. Cunningham, University of California Radiation Laboratory Report UCRL-1220 (1951).

Figure 4. Molar magnetic susceptibilities of some actinide and lanthanide ions. The values of the susceptibilities given by the simple theory at 20°C are 2730, 5420, 5540, 3040, 300, 0, 27250, multiplied by 10^{-6}.(Data from Ref. 48, 49, 50).

Crane and Cunningham[50] have measured the molar magnetic susceptibility of solid CmF_3 in 10 mole percent solid LaF_3 and have found the value to be 26,500 ± 700 x 10^{6} c.g.s. units at about 20° C which is a very large



MOLAR MAGNETIC SUSCEPTIBILITY e.m.u. × 10^6
NUMBER OF f ELECTRONS
1000
2000
3000
4000
5000
26,000
27,000
1
2
3
4
5
6
7
Ce(III)
Pr(III)
Nd(III)
Pm(III)
Sm(III)
Eu(III)
Gd(III)
Np(VI)
Np(V)
Np(IV)
Pu(IV)
Pu(III)
Am(III)
Cm(III)
MU 1651

Figure 4

value in good agreement with the value expected for the ground state term $^8S_{7/2}$ in curium(III). The similarity of curium(III) in this respect to its lanthanide homologue gadolinium(III) is striking (see Figure 4).

Sharp departures from the theoretical susceptibilities occur in both series for the ions with 5 and 6 unpaired electrons. The $^7F_0$ ground state term for europium(III) and for americium(III) should lead to zero magnetic moment; instead, the rather high values listed in Figure 4 are found. The theoretical value for the $^6H_{5/2}$ ground state term for samarium(III) and plutonium(III) is 300 x 10^6 units. The discrepancy in the case of samarium and europium was resolved completely by Van Vleck and Frank[51] who showed that the multiplet splitting in these cases is comparable to kT; equation 10.1 above is based on the assumption, not previously stated, that multiplet splitting is large compared to kT, i.e., that only the ground state term contributes to the magnetism. When allowance is made for the contribution of other terms of the multiplet, good agreement is obtained with experiment. This correction is unimportant for the other lanthanide ions. In the case of plutonium(III) and americium(III) the analogous calculation has not been made but the lower values of the susceptibilities of these ions presumably indicate wider multiplet splitting in the actinide ions. Preliminary interpretation of the fluorescence spectrum of americium bears out this deduction.[44]

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[51] J. H. Van Vleck and A. Frank, Phys. Rev. 34, 1494, 1625 (1929).

Another consequence of the Van Vleck and Frank theory is that the susceptibility for samarium should pass through a temperature minimum in the neighborhood of 400° K; such a minimum has been observed experimentally. Elliott and Lewis[52] made measurements on PuF_3 and $Pu_2(C_2O_4)_3 \cdot 9H_2O$ from 76-300° K. Dawson, Mandlebeg and Lewis[53] extended measurements on PuF_3 and $PuCl_3$ up to about 600° K and found a minimum in the susceptibility-temperature curve at about 500-555° K. This is good qualitative evidence that plutonium(III) has the electron configuration $5f^5$.

Susceptibility measurements have been made on a large number of uranium(IV) compounds by many authors.[54-69] The results lie in the range 3,200 to 3,800 x 10^{-6} units (at room temperature) which is closer to the $6d^2$

spin-only value of 3333 than to the limiting $5f^2$ value of 5,390. The behavior of the susceptibility of $U(SO_4)_2 \cdot 3.26H_2O$ and of $U(C_2O_4)_2 \cdot 5H_2O$ over a wide range of temperature, however, caused Hutchison and Elliott[55] to conclude that uranium(IV) was isoelectronic with praseodymium(III). They also concluded that the crystal fields produce more pronounced perturbing effects on uranium(IV) than on praseodymium(III). On the other hand the magnetic measurements of Dawson and Lister[57] on UO_2 and uranium tetrafluoride diluted with diamagnetic thorium tetrafluoride are interpreted by Dawson[59] to indicate the configuration $6d^2$ for uranium(IV). Similarly, Trzebiatowski and Selwood[58] feel that their measurements on solid dilute solutions of uranium dioxide in diamagnetic thorium dioxide are best interpreted in terms of 6d electrons in uranium(IV) since the value at infinite dilution corresponds to complete quenching of the orbital contribution; similar experiments by Dawson and Lister[69] and Slowinski and Elliott[68] lead to the same result. This seems reasonable since uranium is in just the region where the energy difference between the 5f and 6d levels seems to be within the range of chemical binding energies; however, since the argument for the $6d^2$ configuration is based on the observed quenching of the orbital contribution to the magnetic moment the possibility of this occurring with 5f electrons should be studied further.

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[52] N. Elliott and W. B. Lewis, Abstract 90, reported at the 118th meeting of the American Chemical Society, Chicago, Illinois, September 1950; Report AECD-29100 (1950).

[53] J. K. Dawson, C. J. Mandleberg, and D. Davies, J. Chem. Soc. 2047 (1951).

[54] W. Sucksmith, Phil. Mag. 14, 1115 (1935).

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[59] J. K. Dawson, J. Chem. Soc. 2889 (1951); 1185 (1952).

[60] N. Elliott, Phys. Rev. 76, 431 (1949).

[61] J. K. Dawson, J. Chem. Soc. 429 (1951).

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[63] H. Haraldsen and R. Bakken, Naturwissenschaften 28, 127 (1940).

[64] H. Bommer, Z. anorg. Chem. 247, 249 (1941).

[65] N. Elliott, L. Corliss and Y. Delabarre, Brookhaven National Laboratory Report BNL-39 (AS-3) p. 47, December 1949.

[66] R. Stoenner and N. Elliott, J. Chem. Phys. 19, 950 (1951).

[67] N. Elliott and W. B. Lewis, U. S. Atomic Energy Commission Document, AECD-2910, 1950.

[68] E. Slowinski and N. Elliott, Brookhaven National Laboratory Report, BNL-1199.

[69] J. K. Dawson and M. W. Lister, J. Chem. Soc. 5041 (1952).

A number of measurements have been made on plutonium(IV) compounds in which four unpaired electrons may be expected.[48, 70, 71] Dawson has evidence that the paramagnetic electron-exchange interaction contributes materially to a lowering of the susceptibility. He made measurements on plutonium tetrafluoride and plutonium dioxide diluted with the isostructural diamagnetic compounds thorium tetrafluoride and thorium dioxide, respectively, and found susceptibilities increasing with dilution, with the extrapolated values at infinite dilution for room temperature (3020×10^{-6}) corresponding essentially to the value predicted (3010×10^{-6}) for the configuration $5f^4$.

The neptunyl ion contains one unpaired electron and the plutonyl ion contains two. Several measurements of the magnetic susceptibility of compounds such as sodium neptunyl acetate[72, 73] and sodium plutonyl acetate[74] have been carried out. Detailed theoretical analysis of Elliott[75] and of Eisenstein and Pryce[76] has shown that the susceptibility is strongly influenced by the special properties of the linear $[\text{O-Np-O}]^{+2}$ and $[\text{O-Pu-O}]^{+2}$ ions and that the measured low values for the susceptibility are completely consistent with the presence of 5f electrons. This theoretical analysis modifies previous interpretations of the data on these ions.[77, 78]

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[70] J. K. Dawson, J. Chem. Soc. 1882 (1952).

[71] N. Elliott, W. B. Lewis, Paper 90, Symposium on "The Chemistry of the Actinide Elements", American Chemical Society Meeting, Chicago, September, 1950.

[72] D. M. Gruen, Argonne National Laboratory Report ANL-4469, June (1950).

[73] D. M. Gruen and C. A. Hutchison, Jr., J. Chem. Phys. 22, 386 (1954).

[74] J. K. Dawson, Atomic Energy Research Establishment Report AERE C/R-876 (1952).

[75] R. J. Elliott, Phys. Rev. 89, 659 (1953).

[76] J. C. Eisenstein and M. H. L. Pryce, Proc. Roy. Soc. (A), 229: 20 (1955).

[77] J. K. Dawson, Nucleonics 10 (9) 39 (1952).

[78] J. K. Dawson and G. R. Hall Paper, "Peaceful Uses of Atomic Energy - Proceedings of the Geneva Conference", P/440, August, 1955, United Nations.

Predictions of the theory[76] regarding anisotropic susceptibility in single crystals have been confirmed by paramagnetic resonance experiments.[79, 80] The presence of a single 5f electron in NpO_2^{+2} and of two 5f electrons in PuO_2^{+2} may be considered to be definitely established.

Gruen, Malm and Weinstock[81] measured the magnetic molal susceptibility of crystalline plutonium hexafluoride and found the value 290×10^{-6} at 295° K and 330×10^{-6} at 81° K. This small, relatively temperature-independent susceptibility is surprising since other compounds that are isoelectronic with PuF_6(U^{+4}, NpO_2, and PuO_2^{+2}) have susceptibilities of magnitude $3000 - 4000 \times 10^{-6}$ at room temperature that are strongly temperature dependent. It seems likely that the two non-bonding electrons in PuF_6 unlike those in U^{+4}, NpO_2^{+1}, and PuO_2^{+2} have paired spins and that the electronic ground state is non-degenerate.

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[79] B. Bleaney, P. M. Llewellyn, M. H. L. Pryce, and G. R. Hall, Phil. Mag. 45, 773, 991 (1954); 45, 992 (1954).

[80] C. A. Hutchison, Jr., and W. B. Lewis, Phys. Rev. 95, 1096 (1954).

[81] D. M. Gruen, J. G. Malm, and B. Weinstock, unpublished results cited by B. Weinstock and J. G. Malm, paper P/733, "Peaceful Uses of Atomic Energy - Proceedings of the Geneva Conference", August, 1955, United Nations.

In summary, the interpretation of experimental data has shown that the predictions of the actinide concept are borne out in the following ions:

$Cm^{+3}(5f^7)$; $Am^{+3}(5f^6)$; $Pu^{+3}(5f^5)$; $Pu^{+4}(5f^4)$; NpO_2^{+1}, $PuO_2^{+2}(5f^2)$; $NpO_2^{+2}(5f^1)$ and $UO_2^{+2}(5f^0)$. In the case of U^{+4} (two unpaired electrons) and U^{+3} (three unpaired electrons) many workers have interpreted the data in support of 6d electrons, but a final decision has not been made. In the case of Th^{+3} (one unpaired electron) and Th^{+2} (two unpaired electrons) the evidence strongly favors a 6d assignment. These results are consistent with the chemical evidence in indicating that the 6d and 5f levels are of equivalent energy in the first few elements of the series, but that the f electron levels definitely lie lower once these elements are passed. The magnetic evidence is perhaps the most definite in showing the presence of f electrons in neptunium and plutonium.

12. <u>Spectroscopic data</u>. Spectroscopic data yield detailed information on the electron configurations of the lowest-lying states for the gaseous atoms for a few of the actinide elements. Such data lends strong support to the actinide concept. Kiess, Humphreys, and Laun[81a] observed the spectra of uranium under arc and spark excitation and catalogued 9000 lines in the UI spectrum with accurate wavelengths and estimated intensities for the region 2900 Å to 11,000 Å. With the aid of well resolved Zeeman patterns the authors determined that the lowest lying term was $^5L_6$ $(5f^3 6d^1 7s^2)$. Other important low-lying terms are $^5K_5(5f^3 6d 7s^2)$ and $^7M_6(5f^3 6d^2 7s)$ with the three 5f electrons appearing throughout. Schuurmans and co-workers confirm this analysis of UI and provide an analysis of the UII spectrum. The lowest-lying term is $^4I_{9/2}(5f^3 7s^2)$. All important low levels are ascribed to configurations with three 5f electrons; namely $(5f^3 7s^2)(5f^3 6d 7s)$ and $(5f^3 6d^2)$. The important terms are ^4I, ^6L, ^6K, ^6M, and ^6I. Additional work on UII has been carried out by McNally and Harrison[84, 85] and by van den Bosch.[86] The information which has been deduced by the analysis of these workers is extensive, but a complete analysis of the exceedingly complex spectra of uranium will require much additional work. The present analysis is very strong evidence for the conception of uranium as the third actinide element analogous to neodymium in the rare-earth series. The term analysis of neodymium spectra[87] however, leads to somewhat different results for the ground state terms. In NdI the only ground state term identified was $4f^4 6s^2 (^5I)$. In NdII the low-lying levels and configurations are $4f^4 6s(^6I$ and $^4I)$ and $4f^4 5d(^6L\,^6K)$; the ground state term is $^6I_{7/2}$.

[81a] C. C. Kiess, C. J. Humphreys, and D. D. Laun, J. Research Nat. Bur. Standards, 37, 57 (1946); J. Opt. Soc. Amer. 36, 357 (1946).

[82] P. Schuurmans, Physica 11, 419 (1946).

[83] P. Schuurmans, J. C. van den Bosch, and N. Dijkwel, Physica 13, 117 (1947).

[84] J. R. McNally, Jr., and G. R. Harrison, Report Y-340 (1949).

[85] J. R. McNally, Jr., Phys. Rev. 77, 417 (1950).

[86] J. C. van den Bosch, Physica 15, 503 (1949); Phys. Rev. 80, 100 (1950).

[87] W. E. Albertson, Astrophys. J. 84, 26 (1936).

In the case of thorium, two groups of investigators[88, 89] have interpreted the spectrum of Th(II) due to singly ionized thorium atoms. The lowest-lying energy states belong to ($6d7s^2$), ($6d^27s$), and ($6d^3$) electron configurations. A set of prominent low-lying states, however, are attributed to the configurations ($5f7s^2$) and ($5f6d7s$).

Additional observations on the gaseous Th^{+2} and Th^{+3} spectra[90-94] show that 6d and 5f electrons are close in energy. For example, the ground level of Th(III) is $^3F_2(6d^2)$ while the level $^3H_4(5f6d)$ lies only 809.9 cm^{-1} above.[90]

In the case of the transuranium elements the results from uranium spectra have been used, in lieu of additional information, to make predictions concerning the expected electronic configuration for the neutral gaseous atoms.[95] More recent experimental information has necessitated changes in these configurations which reflect a closer similarity to the corresponding lanthanide elements than had been expected.

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[88] J. R. McNally, G. R. Harrison, and H. B. Park, J. Opt. Soc. Am. 32, 334 (1942); J. R. McNally, Jr., J. Opt. Soc. Am. 35, 390 (1945).

[89] T. L. deBruin, P. Schuurmans, and P. F. A. Klinkenberg, Z. Physik 121, 667 (1943); 122, 23 (1944).

[90] P. F. A. Klinkenberg, Physica 16, 618, 185 (1950);

[91] R. J. Lang, Can. J. Research, A14, 43 (1946).

[92] T. L. deBruin and P. F. A. Klinkenberg, Proc. Acad. Sci. Amsterdam 43, 581 (1948).

[93] T. L. de Bruin, P. F. A. Klinkenberg, and P. Schuurmans, Z. Physik 118, 58 (1941).

[94] P. F. A. Klinkenberg and R. J. Lang, Physica 15, 774 (1949).

[95] W. F. Meggers, Science 105, 514 (1947).

Work on the Zeeman effect in plutonium[96] spectra indicated a prominent $^6F(5f^7 7s)$ state for PuII. An extended analysis by McNally[97] showed that the ground state of PuII was $^8F_{1/2}(5f^6 7s^1)$ with $^8F_{3/2}$ lying 2014.7 cm^{-1} above. This ground state is identical to that of SmII,[98] the rare earth homologue of plutonium. One may predict that the ground state of PuI is $^7F(4f^6 6s^2)$ by analogy to SmI.

A preliminary term analysis of the spectrum of americium by Fred and Tomkins[99] establishes the ground state of AmII as $^9S(4f^7 6s^1)$ with the splitting between the ^9S and the ^7S multiplet equal to 2498.35 cm^{-1}. This compares to 1669.21 cm^{-1} for the same multiplet splitting in EuII. Hence the ground state of AmI is probably $^8S(4f^7 6s^2)$, similar to that of EuI.

The rare earth homologue of curium is gadolinium. The ground state[98] of GdI is $^9D(4f^7 5d^1 6s^2)$ and of GdII is $^{10}D(4f^7 5d^1 6s^1)$. There are six multiplets lying below 11,000 cm^{-1} and the highest two of these are inverted.

$^{10}D(4f^7 5d^1 6s^1)$
$^8D(4f^7 5d^1 6s^1)$
$^8S(4f^7 5d^1 6s^1)$
$^{10}F(4f^7 5d^1 6s^1)$
$^8D(4f^7 5d^1 6s)$ inverted
$^6D(4f^7 5d^1 6s)$ inverted

The optical spectrum of curium has been observed[100] but no term analysis has been carried out. The isotope shift has been studied[101] using samples of Cm^{242} and Cm^{244}. A shift was observed in 148 lines out of 182 recorded with shifts ranging up to 0.131 cm^{-1}. For some lines the shifts are opposite in sign to those of the majority. These observations constitute qualitative evidence for an electronic configuration in curium similar to gadolinium. The large isotope shift observed for several of the actinide elements is believed to be associated with s^1 and s^2 electrons.

Six multiplets near the ground state would explain why such a large percentage of lines show the isotope shift. Inverted multiplets could account for the shifts in the abnormal direction.

Thus the recent work on plutonium, americium, and curium suggests that these elements are following a pattern similar to samarium, europium, and gadolinium. The succeeding actinide elements in lieu of any experimental information other than chemical information, are shown in Table I, Section 2, with electron configurations analogous to the rare earths.

Figure 5 is a periodic chart of the elements with the elements above actinium grouped as an actinide series.

Figure 5. Periodic chart of the elements.

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[96] P. M. Griffin and J. R. McNally, Jr., J. Opt. Soc. Am. 45, 63 (1955).

[97] J. R. McNally, Jr., J. Opt. Soc. Am. 45, 901 (1955).

[98] H. N. Russell, J. Opt. Soc. Am. 40, 550 (1950).

[99] M. Fred and F. S. Tomkins, J. Opt. Soc. Am. 44, 824 (1954).

[100] J. G. Conway, M. F. Moore and W. W. T. Crane, J. Am. Chem. Soc. 73, 1308 (1951).

[101] J. G. Conway and R. D. McLaughlin, J. Opt. Soc. Am. 46, (1956).

B. THE INDIVIDUAL ELEMENTS

I. NEPTUNIUM (ELEMENT 93)

a. History of Neptunium

13. <u>The transuranium elements before the discovery of fission.</u> Not long after the discovery of the neutron Fermi[1] realized that the bombardment of uranium by neutrons might be expected to lead to the production of one or more radioactive isotopes of uranium which would decay to form atoms of element 93. This prediction was eventually proved to be correct and it is now known that Np^{239} can be produced by the following sequence when uranium is irradiated with slow neutrons.

$$U^{238}\ (n, \gamma)\ U^{239};\quad U^{239}\ \xrightarrow[\beta^-]{23.5\text{ min.}}\ Np^{239} \tag{13.1}$$

When fast neutrons are used Np^{237} is produced via the sequence:

$$U^{238}\ (n, 2n)\ U^{237};\quad U^{237}\ \xrightarrow[\beta^-]{6.7\text{ days}}\ Np^{237} \tag{13.2}$$

These facts were not determined for many years, however, because between 1934 and the time of the careful radiochemical experiments of Hahn and Strassmann[2] published in 1939, it was not realized that nuclear fission occurred when uranium was bombarded with slow neutrons. Many of the fission product activities were incorrectly considered to be transuranium element isotopes. The situation was further confused experimentally by the belief that element 93 should resemble rhenium, that element 94 should resemble osmium, etc. A rather extensive literature developed on the "transuranium" elements 93-96 in the period immediately before the discovery of fission. An historical account is given by Turner.[3] The interesting but confusing experimental results which had become so difficult to understand from the standpoint of known physics or chemistry were quickly and correctly interpreted in terms of fission product activities when the phenomenon of nuclear fission was recognized.

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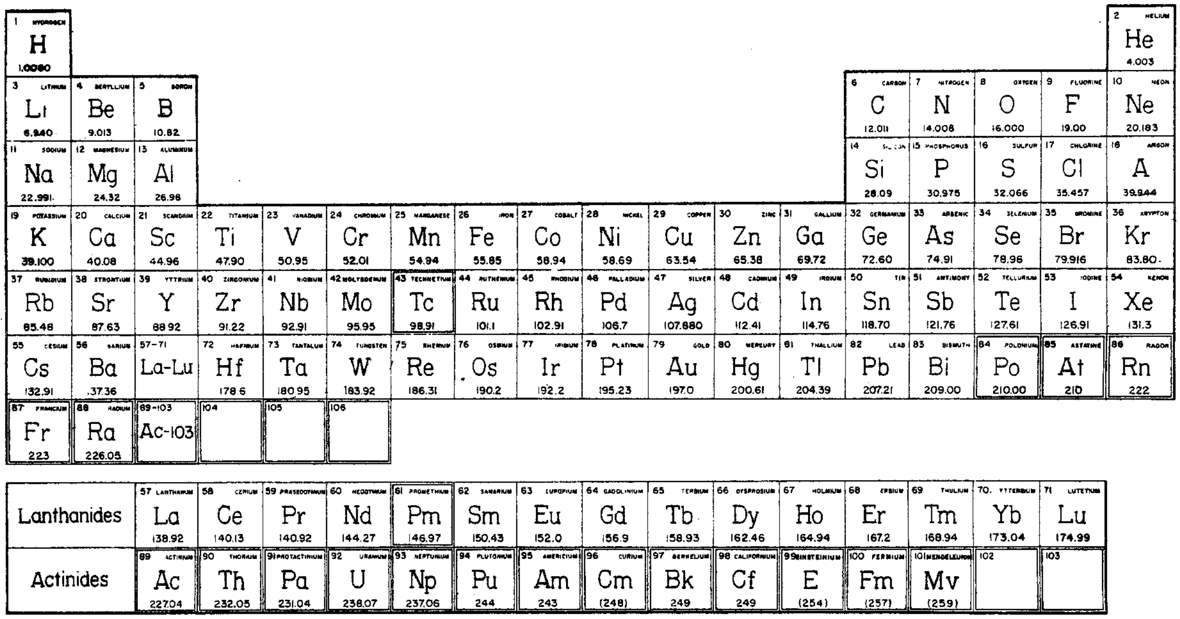
[1] E. Fermi, Nature <u>133,</u> 898 (1934).

[2] O. Hahn and F. Strassmann, Naturwiss <u>27,</u> 163 (1939).

[3] L. A. Turner, Rev. Mod. Physics <u>12,</u> 1 (1940).



1 HYDROGEN H 1.0080																	2 HELIUM He 4.003
3 LITHIUM Li 6.940	4 BERYLLIUM Be 9.013	5 BORON B 10.82											6 CARBON C 12.011	7 NITROGEN N 14.008	8 OXYGEN O 16.000	9 FLUORINE F 19.00	10 NEON Ne 20.183
11 SODIUM Na 22.991	12 MAGNESIUM Mg 24.32	13 ALUMINUM Al 26.98											14 SILICON Si 28.09	15 PHOSPHORUS P 30.975	16 SULFUR S 32.066	17 CHLORINE Cl 35.457	18 ARGON A 39.944
19 POTASSIUM K 39.100	20 CALCIUM Ca 40.08	21 SCANDIUM Sc 44.96	22 TITANIUM Ti 47.90	23 VANADIUM V 50.95	24 CHROMIUM Cr 52.01	25 MANGANESE Mn 54.94	26 IRON Fe 55.85	27 COBALT Co 58.94	28 NICKEL Ni 58.69	29 COPPER Cu 63.54	30 ZINC Zn 65.38	31 GALLIUM Ga 69.72	32 GERMANIUM Ge 72.60	33 ARSENIC As 74.91	34 SELENIUM Se 78.96	35 BROMINE Br 79.916	36 KRYPTON Kr 83.80
37 RUBIDIUM Rb 85.48	38 STRONTIUM Sr 87.63	39 YTTRIUM Y 88.92	40 ZIRCONIUM Zr 91.22	41 NIOBIUM Nb 92.91	42 MOLYBDENUM Mo 95.95	43 TECHNETIUM Tc 98.91	44 RUTHENIUM Ru 101.1	45 RHODIUM Rh 102.91	46 PALLADIUM Pd 106.7	47 SILVER Ag 107.880	48 CADMIUM Cd 112.41	49 INDIUM In 114.76	50 TIN Sn 118.70	51 ANTIMONY Sb 121.76	52 TELLURIUM Te 127.61	53 IODINE I 126.91	54 XENON Xe 131.3
55 CESIUM Cs 132.91	56 BARIUM Ba 137.36	57–71 La-Lu	72 HAFNIUM Hf 178.6	73 TANTALUM Ta 180.95	74 TUNGSTEN W 183.92	75 RHENIUM Re 186.31	76 OSMIUM Os 190.2	77 IRIDIUM Ir 192.2	78 PLATINUM Pt 195.23	79 GOLD Au 197.0	80 MERCURY Hg 200.61	81 THALLIUM Tl 204.39	82 LEAD Pb 207.21	83 BISMUTH Bi 209.00	84 POLONIUM Po 210.00	85 ASTATINE At 210	86 RADON Rn 222
87 FRANCIUM Fr 223	88 RADIUM Ra 226.05	89–103 Ac-103	104	105	106												

Lanthanides	57 LANTHANUM La 138.92	58 CERIUM Ce 140.13	59 PRASEODYMIUM Pr 140.92	60 NEODYMIUM Nd 144.27	61 PROMETHIUM Pm 146.97	62 SAMARIUM Sm 150.43	63 EUROPIUM Eu 152.0	64 GADOLINIUM Gd 156.9	65 TERBIUM Tb 158.93	66 DYSPROSIUM Dy 162.46	67 HOLMIUM Ho 164.94	68 ERBIUM Er 167.2	69 THULIUM Tm 168.94	70. YTTERBIUM Yb 173.04	71 LUTETIUM Lu 174.99
Actinides	89 ACTINIUM Ac 227.04	90 THORIUM Th 232.05	91 PROTACTINIUM Pa 231.04	92 URANIUM U 238.07	93 NEPTUNIUM Np 237.06	94 PLUTONIUM Pu 244	95 AMERICIUM Am 243	96 CURIUM Cm (248)	97 BERKELIUM Bk 249	98 CALIFORNIUM Cf 249	99 EINSTEINIUM E (254)	100 FERMIUM Fm (257)	101 MENDELEVIUM Mv (259)	102	103

MU-[illegible]

Figure 5

14. The discovery of neptunium - summary of known isotopes. Following the discovery of fission and the realization that most of the activities produced in the bombardment of uranium with slow neutrons were fission products rather than transuranium elements a new search was begun for element 93. The first certain identification of an isotope of this element was carried out by McMillan and Abelson[4] at the University of California in 1940; they found the 2.3-day isotope Np^{239} formed as the decay product of the 23-minute U^{239} produced from the bombardment of uranium with neutrons; $U^{238}(n, \gamma)U^{239} \xrightarrow[\text{23 minutes}]{\beta^-} Np^{239}$. McMillan and Abelson chose the name neptunium (symbol Np) from the planet Neptune which is the first planet beyond Uranus in our solar system. McMillan and Abelson realized from their chemical experiments that this first transuranium element was not eka-rhenium and that it must be a member of a 5f transition series.

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[4] E. M. McMillan and P. H. Abelson, Phys. Rev. 57, 1185 (1940).

When uranium was bombarded with deuterons in the Berkeley 60-inch cyclotron 2.3-day Np^{239} was produced by the (d, n) reaction, and in addition, another isotope, 2.0-day Np^{238}, was produced.[5] Much of the initial tracer work on neptunium chemistry was performed with Np^{239} produced by neutron irradiation of uranium or with the Np^{239}-Np^{238} mixture produced by deuteron bombardment of uranium.

The longest-lived isotope of neptunium and the isotope which must be regarded as the most important from the standpoint of chemistry is Np^{237} which has a half-life of 2.2×10^6 years. It was found by Wahl and Seaborg in 1942,[6] and is produced by the reaction

$$U^{238}(n, 2n)U^{237} \xrightarrow[\text{6.75 days}]{} Np^{237} \qquad (14.1)$$

The first isolation of a weighable amount of Np^{237} was carried out by Magnusson and La Chapelle[7] at the Metallurgical Laboratory in October, 1944. The operation of large nuclear reactors for the production of plutonium has made it possible to isolate many grams of neptunium because it is produced as a by-product by the (n, 2n) reaction. The cross-section for this reaction is approximately one percent of the neutron capture cross-section of U^{238}.

Neptunium-237 has another significance in that it can be regarded as the parent of the 4n+1 radioactive series missing in nature. The other three series, the thorium series (4n), the uranium - radium series (4n+2), and the actinium series (4n+3) are present in nature because the parent activities Th^{232}, U^{238}, and U^{235}, respectively, are sufficiently long-lived to have persisted through geologic time. The half-life of Np^{237} is about a factor of ten too short for the survival of an appreciable fraction of the neptunium which almost certainly was present at the beginning of the world.

It was predicted[8] that very small amounts of Np^{237} must be present in nature due to its continuous production by the action of naturally occurring fast neutrons via reaction (14.1). Peppard and his co-workers[9] have established the existence of Np^{237} in Belgian Congo pitchblende in concentration corresponding to a ratio of Np^{237} to U^{238} of 1.8×10^{-12}.

The 4n+1 series is sometimes called the neptunium series by analogy to the uranium and thorium series.

The neptunium series decay sequence is shown in Figure 6.

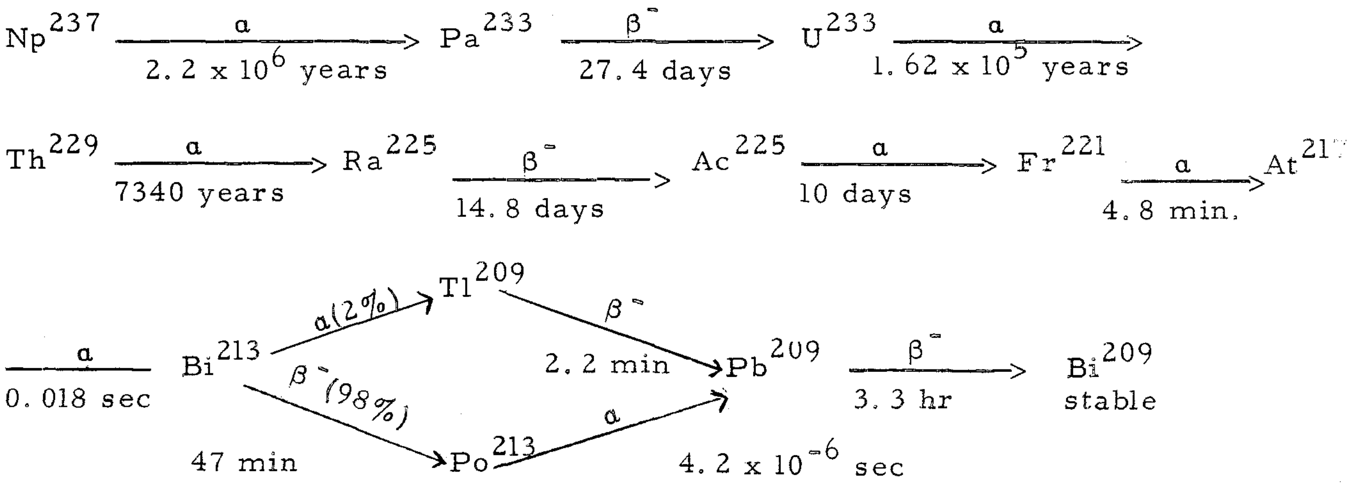

Figure 6. Decay scheme of the neptunium series.[10, 11]

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[5] G. T. Seaborg, A. C. Wahl, and J. W. Kennedy, Paper 1.4, N.N.E.S., Vol. 14B "The Transuranium Elements", 1949.

[6] A. C. Wahl and G. T. Seaborg, Phys. Rev. 73, 940 (1948).

[7] L. B. Magnusson and T. J. LaChapelle, J. Am. Chem. Soc. 70, 3534 (1948); see also Paper 1.7 N.N.E.S. Vol. 14B, "The Transuranium Elements", (1949).

A large additional number of neptunium isotopes have been prepared by cyclotron reactions. These isotopes are listed in Table 7. The decay scheme of those isotopes which have received most careful study are given in Figure 7. Nuclear properties of the transuranium elements as a group will be reviewed in Part C of this report.

Figure 7. Decay schemes of neptunium isotopes.

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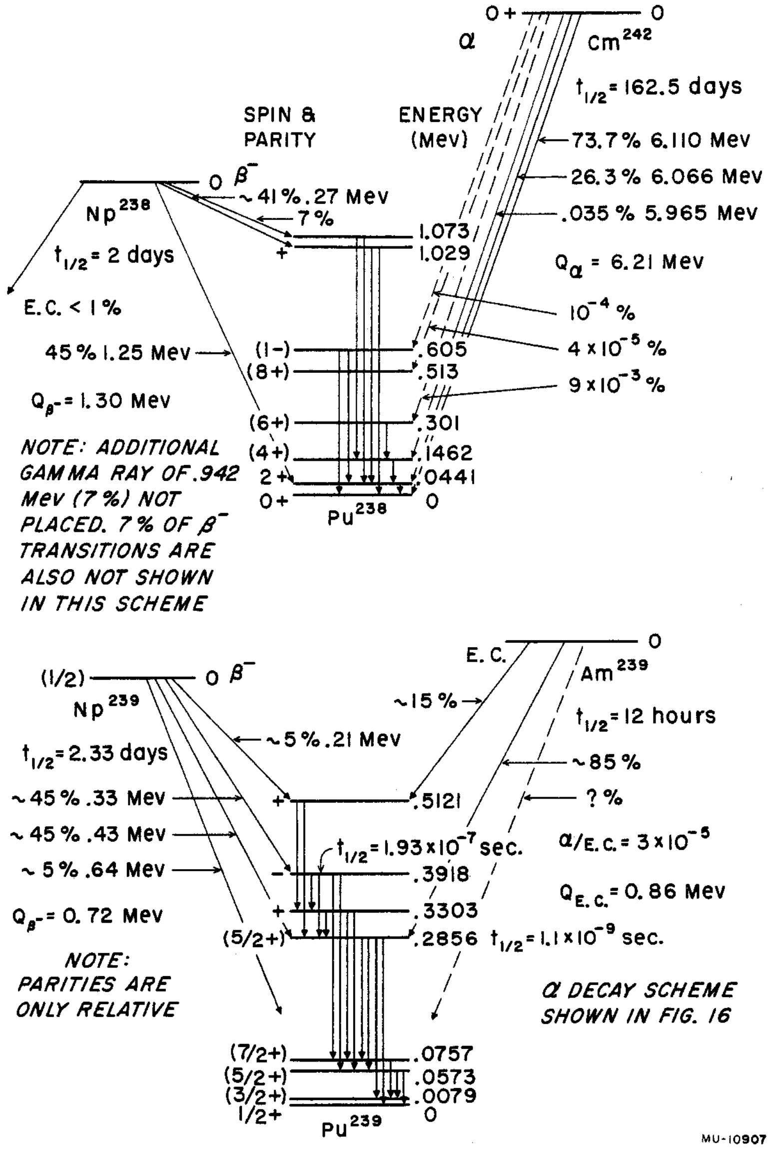
[8] G. T. Seaborg, Chem. Eng. News 25, 358 (1947).

[9] D. F. Peppard, G. W. Mason, P. R. Grey, and J. F. Mech, J. Am. Chem. Soc. 74, 6081 (1952).

[10] F. Hagemann, L. I. Katzin, M. H. Studier, G. T. Seaborg, and A. Ghiorso, Phys. Rev., 79, 435 (1950).

[11] A. C. English, T. E. Cranshaw, P. Demers, J. A. Harvey, E. P. Hincks, J. V. Jelley, and A. N. May, Phys. Rev., 72, 253 (1947).



α
0+
0
Cm^{242}
$t_{1/2}$= 162.5 days
SPIN & PARITY
ENERGY (Mev)
73.7 % 6.110 Mev
26.3 % 6.066 Mev
.035 % 5.965 Mev
Q_{α} = 6.21 Mev
10^{-4} %
4×10^{-5} %
9×10^{-3} %
0 β$^-$
Np^{238}
~41 % .27 Mev
7 %
1.073
+
1.029
$t_{1/2}$= 2 days
E.C. < 1 %
45 % 1.25 Mev
(1−) .605
(8+) .513
Q_{β^-} = 1.30 Mev
(6+) .301
(4+) .1462
2+ .0441
0+ 0
Pu^{238}
NOTE: ADDITIONAL GAMMA RAY OF .942 Mev (7 %) NOT PLACED. 7 % OF β$^-$ TRANSITIONS ARE ALSO NOT SHOWN IN THIS SCHEME
E.C.
0
Am^{239}
(1/2)
0 β$^-$
Np^{239}
~15 %
$t_{1/2}$= 12 hours
~5 % .21 Mev
$t_{1/2}$= 2.33 days
~85 %
~45 % .33 Mev
+ .5121
? %
~45 % .43 Mev
$t_{1/2}$= 1.93 × 10^{-7} sec.
α/E.C. = 3 × 10^{-5}
~5 % .64 Mev
− .3918
$Q_{E.C.}$= 0.86 Mev
Q_{β^-} = 0.72 Mev
+ .3303
(5/2+) .2856 $t_{1/2}$= 1.1 × 10^{-9} sec.
NOTE: PARITIES ARE ONLY RELATIVE
α DECAY SCHEME SHOWN IN FIG. 16
(7/2+) .0757
(5/2+) .0573
(3/2+) .0079
1/2+ 0
Pu^{239}
MU-10907

Figure 7

Table 7 Isotopes of Neptunium*

Isotope and Half-Life	Type of Decay	Energy (Mev)	Method of Production	Disintegration** Energies (Mev)
Np^{231} 50m	α	6.28	U^{238} d-9n U^{233} d-4n U^{235} d-6n	Q_{α} =6.39 Q_{EC}=1.82(calc.)
Np^{232} 13m	EC γ	hard	U^{233} d-3n	Q_{α} =6.01(est.) Q_{EC}=2.65(est.)
Np^{233} 35m	EC 99^{+}% α 10^{-3}%	5.53	U^{233} d-2n U^{235} d-4n U^{233} p-n	Q_{EC}=1.04(calc.) Q_{α} =5.39(calc.)
Np^{234} 4.4d	EC 99% γ β^{+} $5x10^{-2}$% (Ref. 2)	.78, 1.57(Ref. 1) 0.8	U^{235} d-3n U^{235} α-p4n U^{235} p-2n U^{233} d-n U^{233} α-p2n Pa^{231} d-n	Q_{EC}=1.82(est.) Q_{α} =5.39(calc.)
Np^{235} 410 d	EC L/K=30 α $3.5x10^{-3}$% γ(Ref. 3)	no γ [.085, .026] metastable $t_{1/2}=4x10^{-8}$sec.	U^{235} d-2n U^{233} α-pn	Q_{EC}=0.17(calc.) Q_{α} =5.15
$Np^{236m***}$ >5000 y	β^{-}		U^{238} d-4n	
Np^{236} 22 h	β^{-} 57% γ EC 43% γ	.518(80%), .475(20%)(Ref. 4) .0446(Ref. 5) .0452(Ref. 5)	U^{235} d-n U^{235} α-p2n U^{238} d-4n Np^{237} d-p2n U^{233} α-p Np^{237} n-2n	Q_{β^-} =0.52 Q_{EC}=0.91(calc.) Q_{α} =5.10(calc.)

Isotope and Half-Life	Type of Decay	Energy (Mev)	Method of Production	Disintegration** Energies (Mev)
Np^{237}	α	4.872(3.1%), 4.816(3.5%)	daughter U^{237}	Q_{α}=4.97
2.2×10^{6} y	β stable	4.787(53%), 4.767(29%),	U^{238} (n-2n) U^{237}	I =5/2
		4.713(1.7%), 4.674(3.3%)		
		4.644(6.0%), 4.589(0.5%)		
		4.52(0.02%)(Ref. 6)		
	γ	$.029^{+}$, $.0869^{+}$, .145, .175, .200		
		(Ref. 6)		
		+metastable $t_{1/2}=3.7\times10^{-8}$ sec.		
		.033 and .076 levels in Np^{237}		
		reached by Coulomb excitation.[11]		
Np^{238}	β^{-}	.27, 1.25(Ref. 7)	Np^{237} n-γ	$Q_{\beta^{-}}$ =1.30
2.1d	γ	.044, .1022, .927, .942, .986,	U^{238} d-2n	Q_{EC}=0.12(calc.)
		1.029(Ref. 7)	U^{238} α-p3n	Q_{α} =4.88(calc.)
	EC < 1%		Np^{237} d-p	
Np^{239}	β^{-}	.640, .430, .330, .210(Ref. 8)	U^{238} d-n	$Q_{\beta^{-}}$=0.72
2.33 d β^{-}	γ	.3345, .3165, $.2856^{‡}$, $.2777^{‡}$,	U^{238} α-p2n	Q_{α} =4.56(calc.)
		.2731, .2546, $.2284^{‡}$, .2264,	U^{238} n-$\gamma\beta^{-}$	I =1/2
		$.2090^{‡}$, .1818, $.1061^{+}$, .0678,		
		$.0614^{+}$, .0573, .0494, .0446		
		(Ref. 8)		
		+metastable t 1/2=1.93×10^{-7}sec.		
		‡metastable t 1/2=1.1×10^{-9}sec.		
Np^{240m}	β^{-}	.76(6%), 1.26(11%), 1.59(31%),	daughter U^{240}	$Q_{\beta^{-}}$=2.16
7.3m		2.16(52%)(Ref. 9)		Q_{α} =4.53(est.)
	γ	.56(63%), .90(26%), 1.40(10%)		
		(Ref. 9)		
Np^{240}	β^{-}	.9	U^{238} α-pn	$Q_{\beta^{-}}$=2.05
63m	γ	numerous(Ref. 10)		Q_{α} =4.42(est.)

*For references to original data not given specifically here, refer to Hollander, Perlman and Seaborg, "Table of Isotopes," Rev. of Mod. Physics, 25, 469 (1953) and to the compilations of the Nuclear Data Group, National Research Council.

**Disintegration energies Q are revised values from R. A. Glass, S. G. Thompson, and G. T. Seaborg, J. Inorg. and Nuc. Chem. I, 3 (1955).

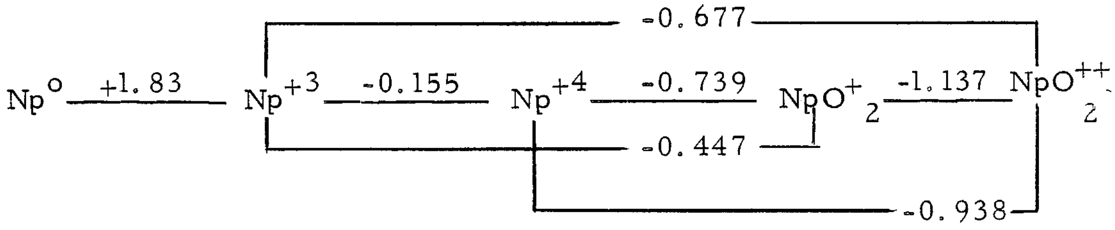
***Placement of Np^{236m} with respect to Np^{236} is not known.

1. R. W. Hoff, Ph.D. Thesis, University of California Radiation Laboratory Report UCRL-2325 (Sept. 1953).
2. R. J. Prestwood et. al., Phys. Rev. 98, 1324 (1955).
3. R. W. Hoff et. al., University of California Radiation Laboratory Report UCRL-4517 (Dec. 1955).
4. T. O. Passell, Ph.D. Thesis, University of California Radiation Laboratory Report UCRL-2528 (1954).
5. J. M. Hollander, private communication (1955).
6. L. B. Magnusson, et. al., Abstract A 11 Bulletin of the American Physical Society, Volume 30, Number 7 (Nov. 1955).
7. J. O. Rasmussen et. al., Phys. Rev. 99, 42 (1955), Phys. Rev. 99, 47 (1955).
8. J. M. Hollander et. al., University of California Radiation Laboratory Report UCRL-3222 (Sept. 1955). Phys.
9. J. D. Knight et. al., Phys. Rev. 91, 889 (1953). Rev. May 1, 1956.
10. R. M. Lessler, University of California Radiation Laboratory Report UCRL-2647 p. 54 (July 1954).
11. J. O. Newton, Nature 175, 1028 (1955).

b. Chemical Properties of Neptunium

15. The oxidation states. Neptunium exhibits interesting and complex chemical properties due to the existence of four oxidation states of roughly comparable thermodynamic stability. These are the III, IV, V, and VI oxidation states. In aqueous solution the ionic species, neglecting hydration, are Np^{+3}, Np^{+4}, NpO^{+}_{2}, and NpO^{+2}_{2}. The formal oxidation potentials for neptunium in perchloric acid are given in Figure 8. Only slight complexing of neptunium ion species occurs in dilute hydrochloric acid and nitric acid so that the same potential scheme holds for these acids with but slight changes. In sulfuric acid and other strong complexing media some of the potentials are markedly changed.

Figure 8. Formal Oxidation Potentials of Neptunium in Perchloric Acid[12]



The potentials of the couples in basic solutions are quite different because of hydrolysis reactions but no reliable data are available.

The oxygenated ion NpO^{+2}_{2} resembles UO^{+2}_{2} and PuO^{+2}_{2}. This structure, as well as the NpO^{+1}_{2} structure, is very stable and persists throughout a wide range of acidity; it is modified only when hydrolysis occurs in solutions of low acidity. This type of ion may be considered unique to the actinide elements and probably results from a special type of hybrid-bond formation involving 5f orbitals.

Oxidation-reduction reactions involving interconversion of Np^{+3} and Np^{+4} are rapid because only an electron transfer is involved. A similar situation holds with respect to the NpO^{+}_{2} - NpO^{+2}_{2} couple. Interconversion of members of these two groups such as oxidation of Np^{+4} to NpO^{+}_{2} involves the breaking or making of Np-O bonds so that such reactions can be quite slow. The study of the kinetics of these reactions constitutes an interesting and important part of neptunium chemistry.

Tables 8 and 9 summarize thermodynamic data for the aqueous ions of neptunium.

Table 8. Values of ΔF, ΔH, and ΔS at 298° K in 1.0 M $HClO_4$ for Oxidation Reactions Involving Neptunium Ions.[12]

Reaction	$\Delta\overline{F}$ kcal $mole^{-1}$	$\Delta\overline{H}$ kcal $mole^{-1}$	$\Delta\overline{S}$ e.u.
$Np^{+3}_{(aq)} + H^+ \rightleftharpoons Np^{+4}_{(aq)} + 1/2H_2$	3.58	-5.7	-31.2
$Np^{+4}_{(aq)} + 2H_2O \rightleftharpoons NpO_2^+(aq) + 3H^+ + 1/2\ H_2$	17.04	35.6	62.3
NpO_2^+ aq $+ H^+ \rightleftharpoons NpO_2^+$ (aq) $+ 1/2\ H_2$	26.23	28.1	6.4

Table 9. Partial Molal Heats and Free Energies of Formation for Neptunium Ions in 1.0 M $HClO_4$ at 298° K.[12]

Reaction	$\overline{\overline{H}}$ kcal $mole^{-1}$	$\overline{\overline{F}}$ kcal $mole^{-1}$
$Np^o + 3H^+ \longrightarrow Np^{+3}(aq) + 3/2H_2$ (g)	-126.9	-126.3
$Np^o + 4H^+ \longrightarrow Np^{+4}(aq) + 2\ H_2$ (g)	-132.6	-122.7
$Np^o + 2H_2O(l) + H^+ \longrightarrow NpO_2{}^+(aq) + 5/2\ H_2(g)$	-97.0	-105.7
$Np^o + 2H_2O(l) + 2H^+ \longrightarrow NpO_2{}^{+2}(aq) + 3H_2$ (g)	-68.9	- 79.5

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[12] D. Cohen and J. C. Hindman, J. Am. Chem. Soc. 74, 4682 (1952)

16. Absorption spectra. The aqueous ions of neptunium are colored; neptunium(III), pale purple; neptunium(IV), yellow-green; neptunium(V) green-blue, and neptunium(VI), pale pink in 1 M $HClO_4$ and dark yellow in 1 M H_2SO_4. These ions have sharp absorption spectra in the visible and near-ultraviolet. These sharp bands are believed to arise from forbidden transitions in the f-shell as was mentioned in Section 9. Figures 9 and 10 show the spectra for the neptunium ions in 1.0 molar perchloric acid. The spectra for neptunium(III), neptunium(IV), and neptunium(V) are sufficiently different that spectrophotometric analysis can be used to identify the oxidation state of a neptunium solution or to determine the composition of a mixture of states. Neptunium(VI) does not show any absorption in the visible; this is expected since it has only one unpaired electron.

Figure 9. Absorption spectra of the neptunium(III) and (IV) ions in 1.0 M $HClO_4$: ——— Np(III), ------Np(IV) From Sjoblom and Hindman.[13]

Figure 10. Absorption spectra of neptunium(V) and (VI) ion in 1.0 M $HClO_4$: ——— Np(VI), -------Np(V). Sjoblom and Hindman.[13]

17. Neptunium(III) in aqueous solution. Neptunium(III) is unstable in aqueous solution in the presence of atmospheric oxygen. However in the presence of an inert atmosphere neptunium can be reduced to neptunium(III) at a mercury pool cathode. Alternatively neptunium can be reduced by hydrogen using a platinum-black catalyst.[13] Neptunium(III) resembles plutonium(III) but very little quantitative information is available on its reactions.

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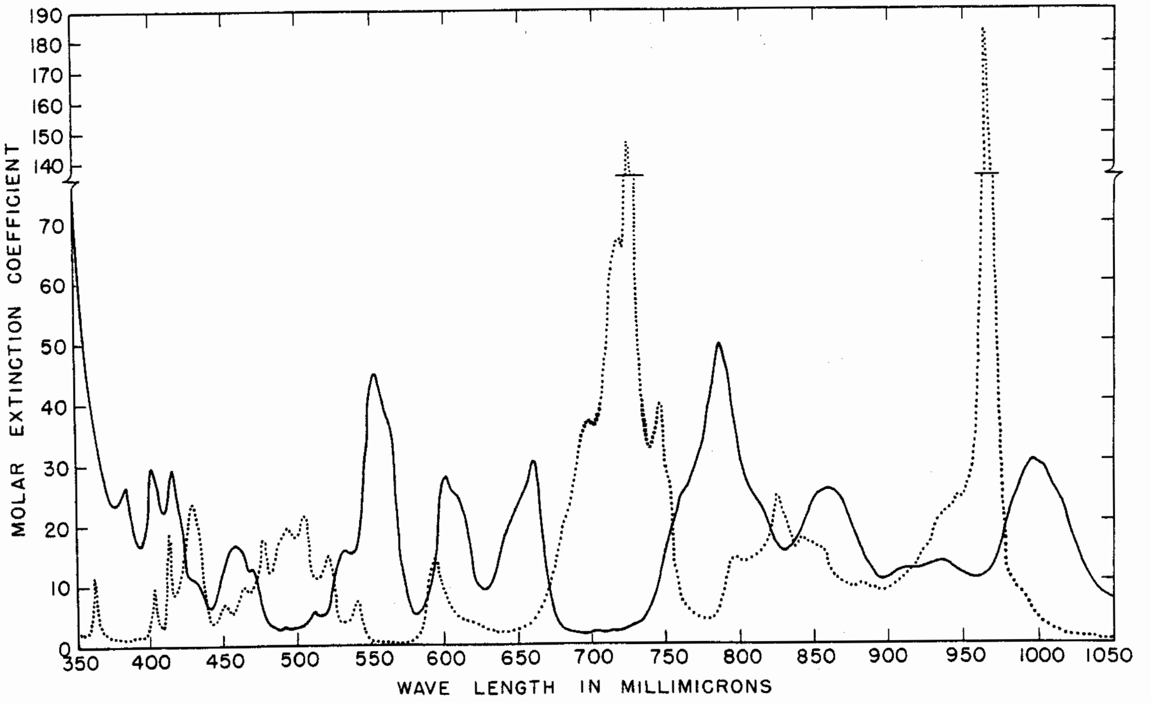
[13] R. K. Sjoblom and J. C. Hindman, J. Am. Chem. Soc. 73, 1744 (1951).

18. Neptunium(IV) in aqueous solution. Neptunium (IV) may be prepared by the reduction of aqueous solutions of neptunium(V) or (VI); in the presence of oxygen no neptunium(III) is found. The reduction to



MU-10958

Figure 9

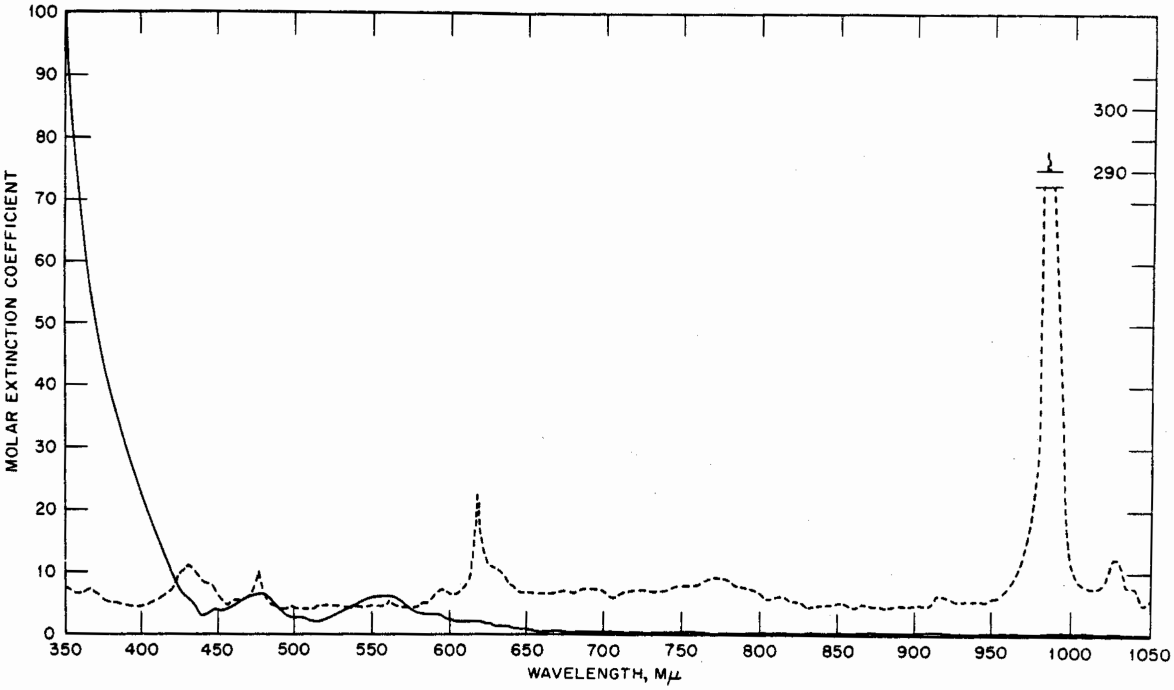


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Figure 10

neptunium(IV) is slow in many instances unless: (1) elevated temperatures are used, (2) a catalyst such as Fe(II) is added, or (3) the (IV) state is stabilized by complexing. Some reagents which are used are potassium iodide and hydrazine in 5 M HCl, hydroxylamine or sulfur dioxide in 1 M sulfuric acid, and stannous ion in 1 M HCl in the presence of iron(II) catalyst.

Neptunium(IV) in 1 M nitric acid is unstable with respect to oxidation by nitrate; in 1 M HCl or 1 M $HClO_4$ it is unstable with respect to oxidation by atmospheric oxygen. In all three solutions, however, the rate of oxidation is slow. In sulfuric acid neptunium(IV) is quite stable because of complex formation. Complexes are also formed with fluoride, phosphate, oxalate, and acetate ions. Complexing of the (IV) state is more pronounced than that of the other oxidation states.

Disporportionation (self-oxidation and reduction) of neptunium(IV) is quite negligible. This is in contrast to the situation in plutonium chemistry.

19. Neptunium(V) in aqueous solution. Neptunium is unique among the actinide elements in having a stable pentapositive state in aqueous solution. Uranium(V) is extremely unstable and prepared only with difficulty. Plutonium(V) is an important aqueous oxidation state of that element but in acidic solution it is unstable toward disproportionation (self-oxidation-reduction to higher and lower oxidation states). Neptunium(V) by contrast is stable in an uncomplexing acidic medium until very high acidities are reached. The disproportionation reaction can be written

$$2\mathrm{Np(V)} \longrightarrow \mathrm{Np(IV)} + \mathrm{Np(VI)}. \qquad K = \frac{[\mathrm{Np(IV)}]\,[\mathrm{Np(VI)}]}{[\mathrm{Np(V)}]^2} \qquad (19.1)$$

The value of the equilibrium quotient, K, has been determined by Sjoblom and Hindman[13] for a variety of acid concentrations. These values are given in Table 10.

Table 10. Value of the disproportionation constant of neptunium(V) as a function of perchloric acid concentration*

Acid Concentration (moles/liter)	$K = \frac{[Np(IV)][Np(VI)]}{[Np(V)]^2}$
1.0	4×10^{-7}
5.34	0.127
7.11	5.78
8.45	169.
8.67	200.

* Data from Sjoblom and Hindman.[13]

Neptunium(V) can be prepared by reduction of neptunium(VI) with hydrazine, iodide, oxalate, sulfite, and tin(II). At room temperature the further reduction of neptunium(V) to neptunium(IV) by these reagents is very slow. Neptunium(V) may also be prepared by heating solutions of neptunium(IV) in 1 M HNO_3 or by stoichiometric oxidation of neptunium(IV) with cerium(IV). Neptunium(V) is oxidized to neptunium(VI) by cerium(IV), silver(II), chlorine, bromate ion and other oxidizing agents. It is rapidly reduced by iron(II) in the presence of nitrous acid.

Neptunium(V) forms no important complexes with chloride, nitrate, perchlorate, or sulfate ion. The weak complexing tendency of NpO_2^+ is in strong contrast to the tendency toward complex formation of NpO_2^{+2}, UO_2^{+2}, and Pu_2^{+2}. Some evidence for complex formation between NpO_2^+ and oxalate ion has been reported.[14] The NpO_2^+ ion does not appear to hydrolyze in solutions of low acidity up to a pH of 5.7. At higher basicity the hydroxide NpO_2OH precipitates.

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[14] D. M. Gruen and J. J. Katz, J. Am. Chem. Soc. 75, 3772 (1953).

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20. Neptunium(VI) in aqueous solution. Neptunium(VI) exists in aqueous solution in the form of the ion NpO_2^{+2} and has a very close resemblance in its properties to UO_2^{+2} and PuO_2^{+2}.

In the presence of strong oxidizing agents such as silver(II), bismuthate ion, bromate ion, cerium(IV), etc., neptunium in its lower oxidation states is converted to neptunium(VI).

Very little quantitative data are available on the complexes of NpO_2^{+2}, but these undoubtedly resemble those of UO_2^{+2} and PuO_2^{+2}.

21. Compounds of Neptunium. Neptunium metal can be prepared by the reduction of neptunium trifluoride or neptunium tetrafluoride with barium metal vapor at 1200° C in a beryllia crucible system.[15] It is a silvery metal melting at 640 ± 1° C. It exists in several forms, an orthorhombic form stable from room temperature to 278 ± 5° C, density 20.45, and a tetragonal β form of density 19.36 stable from 279° to about 550° C where it is believed to undergo transition to a body-centered cubic γ form.[16] Purified hydrogen reacts with neptunium metal at 50° C to yield a black flaky hydride with the composition $NpH_{3.6-3.8}$.[15]

Black or purple hexagonal neptunium trifluoride has been prepared by the reaction:

$$NpO_2(cryst) + 1/2\ H_2(g) + 3HF(g) \xrightarrow{500^\circ\ C} NpF_3(cryst) + 2H_2O(g)$$

In the presence of a mixture of hydrogen fluoride gas and oxygen gas at 500° C the trifluoride is converted to light green monoclinic neptunium tetrafluoride

$$NpF_3(cryst) + 1/4\ O_2(g) + HF(g) \longrightarrow NpF_4(cryst) + 1/2\ H_2O(g).$$

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[15] S. Fried and N. R. Davidson, J. Am. Chem. Soc. 70, 3539 (1948).

[16] W. H. Zachariasen, Acta Cryst. 5, 660 (1952).

Neptunium pentafluoride has never been isolated but should be quite stable.

Neptunium hexafluoride can be prepared by the reaction of neptunium trifluoride with very pure fluorine gas. The trifluoride is supported on a nickel filament heated electrically to red heat. The volatile hexafluoride is condensed on a liquid nitrogen-cooled surface immediately adjacent to the reaction zone before thermal decomposition can occur.

Reddish brown neptunium tetrachloride crystallizing in the tetragonal UCl_4 structure can be prepared by the reaction

$$NpO_2 + CCl_4 \xrightarrow{530^\circ C} NpCl_4 + CO_2.$$

At this temperature neptunium tetrachloride is volatile and sublimes to a cool portion of the apparatus. This volatility is useful in the separation of neptunium and plutonium;[17] when a mixed $NpO_2 - PuO_2$ sample is treated with chlorinating agents a mixture of plutonium trichloride (plutonium does not form a stable tetrachdoride) and neptunium tetrachloride is produced. The neptunium tetrachloride is readily sublimed away from the plutonium trichloride at 500 - 530° C.

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[17] I. K. Shvetsov and A. M. Vorobyev, Paper P/674, "Proceedings of the Geneva Conference - Peaceful Uses of Atomic Energy", August 1955.

Neptunium tetrachloride is reduced to neptunium trichloride by treatment with hydrogen at 450° C. This compound is white and crystallizes in the hexagonal structure. It is volatile at 750 - 800° C.

Neptunium tribromide is a green compound existing in an α hexagonal form and a β orthorhombic form. It has been prepared by reaction of neptunium dioxide with excess aluminum and aluminum tribromide in a sealed tube at 350 - 400° C.

Neptunium tetrabromide is a reddish-brown compound. It has been prepared by heating neptunium dioxide with excess aluminum tribromide in a quartz capillary at 350° C. It sublimes at 500° C.

Neptunium triiodide has been prepared by reacting excess aluminum triiodide with neptunium dioxide in a sealed tube at 350 - 400° C. Neptunium tetraiodide has not been prepared but should be stable.

When neptunium "hydroxide", peroxide, oxalate, or nitrate of any oxidation state are ignited in air to high temperatures neptunium dioxide is formed. Other oxides of neptunium are obtained only under special conditions. Neptunium dioxide is a green compound crystallizing in the face-centered cubic form. Neptunium monoxide has been prepared as a surface coating on neptunium metal. It is semi-metallic in character. Since uranium has an important oxide of the composition U_3O_8, it is interesting that a similar oxide of neptunium has been prepared. Katz and Gruen[18] showed that treatment of various dried hydroxides of neptunium with nitrogen dioxide at 300 - 450° C. resulted in the formation of Np_3O_8, a chocolate-brown solid easily soluble in nitric acid. It

It is isomorphous with U_3O_8. Np_3O_8 is not stable above 500° C. There is no evidence for NpO_3.

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[18] J. J. Katz and D. M. Gruen, J. Am. Chem. Soc. 71, 2106 (1949).

Neptunium forms a colorless, flucculent peroxide compound of low solubility; the formula is $NpO_4 \cdot 2H_2O$ and it is isomorphous with $UO_4 \cdot 2H_2O$.

Neptunium (IV) and (V) are precipitated from alkaline solution as the hydrated "hydroxide" compounds, $(Np(OH)_4 \cdot xH_2O$ and $NpO_2OH \cdot xH_2O$. The solubility of the (IV) hydroxide is a few milligrams per liter from strongly alkaline solutions; that of the (V) hydroxide is considerably greater.

Addition of sodium hydroxide or ammonium hydroxide to aqueous neptunium(VI) solutions results in the precipitation of the dineptunate compounds, $(NH_4)_2Np_2O_7 \cdot H_2O$ and $Na_2Np_2O_7 \cdot H_2O$. These are isostructural with the analogous diuranate compounds.

One of the best known solid compounds of hexavalent neptunium is sodium neptunyl acetate, $NaNpO_2(Ac)_3 \cdot (C_3H_2O_2)_3$. This pink crystalline compound is isostructural with the analogous compounds of uranium, plutonium, and americium.

Additional solid compounds about which structural information is available include neptunium sesquisulfide, neptunium oxysulfide, neptunium dioxyfluoride, neptunium oxydichloride, neptunium nitride, trineptunium tetraphosphide, neptunium(IV) oxalate, and neptunium disilicide.

A detailed treatment of the compounds of neptunium with numerous references to the original literature is given by Cunningham and Hindman.[18a] Lattice constants for a number of crystalline neptunium compounds are given in Table 6, Section 6.

[18a] B. B. Cunningham and J C. Hindman, Chap. 12, N. N. E. S., Vol. 14A "The Actinide Elements".

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22. Coprecipitation behavior of neptunium. Trace concentrations of neptunium can be isolated from aqueous solution by coprecipitation with certain carrier compounds. This coprecipitation can occur even though the solubility product of the related neptunium compound is not exceeded,

but the coprecipitation is most likely to be complete if the carrier compound is similar to a neptunium compound of slight solubility. General types of compounds which are known to "carry" neptunium include the hydroxides, fluorides, phosphates, oxalates, iodates, phenylarsonates, and peroxides. The extent of coprecipitation for most carriers is a function of the oxidation state of neptunium and carriers specific for certain oxidation states can be selected. Radiochemical purification schemes designed to separate neptunium from lighter-element impurities such as the fission products or from neighboring elements invariably depend on the differing behavior of the various oxidation states. These will not be reviewed in detail here, but a few statements will be made about the most important carrier compounds.

Lanthanum fluoride is an excellent carrier for the removal of neptunium(IV) or neptunium(V) from solution. Plutonium in the (III) or (IV) state is also strongly carried. When oxidized to the hexapositive state, neptunium is not carried. In acid solution neptunium(IV) and plutonium(III) can be separated by treatment with bromate ion for 20 minutes at room temperature followed by precipitation of lanthanum fluoride. The plutonium is not oxidized beyond plutonium(IV) because of a slow rate of oxidation, but the neptunium is oxidized to neptunium(VI) which is not precipitated with lanthanum fluoride.

Zirconium phosphate or zirconium phenyl arsonate are good carriers for neptunium or plutonium in the tetrapositive state but leave these elements in solution when they are in the tripositive or hexapositive state. A good neptunium - plutonium separation is achieved by precipitation of one of these carrier compounds after treatment of the solution with a strong reducing agent such as a mixture of hydrazine and iron(II). In the presence of atmospheric oxygen, neptunium is not reduced beyond neptunium(IV), (carried) while plutonium is converted to plutonium(III) (not carried).

Sodium uranyl acetate is an excellent carrier compound for trace amounts of hexavalent neptunium. The lower oxidation states are not carried.

23. Solvent extraction of neptunium. Neptunium(VI) resembles uranium (VI) in being extractable from aqueous solution into certain organic solvents immiscible with water. Ethyl ether has been used extensively in small-scale applications, the extractions usually being performed from nitric acid solutions. To achieve appreciable distribution coefficients into the

ether phase it is necessary to add high concentrations of neutral nitrate salts such as ammonium nitrate or magnesium nitrate to the aqueous phase. This extraction is rather specific and effects purification of neptunium from all but a few elements in the periodic system. Neptunium (VI) can also be extracted into tributylphosphate, dibutyl carbitol, methyl isobutyl ketone, and other solvents of the ketone or "carbitol" or "cellosolve" type.

Neptunium(V) is poorly extracted by ethyl ether and many other organic solvents. Neptunium(IV) is poorly extracted by ethyl ether or methyl isobutyl ketone. It is moderately well extracted by tributyl phosphate, diluted to a 15-30 percent solution in some other organic solvent such as carbon tetrachloride or kerosene, when the aqueous phase has a high concentration of nitrate salts. Detailed information on the extraction of neptunium has not been published. In general the extractability of the hexapositive actinide element ions into organic solvents increases in the order $PuO_2^{+2} < NpO_2^{+2} < UO_2^{+2}$. For the tetrapositive ions the order is $Th^{+4} < Np^{+4} < Pu^{+4}$.

The differing behavior of the various oxidation states can be useful in making a separation of two neighboring actinide elements. For example, if an ether solution of hexapositive uranium and neptunium is contacted with a saturated ammonium nitrate solution containing 0.1 $\underline{M}$ HNO_3 and a small amount of iron(II) and urea the neptunium(VI) is rapidly reduced to neptunium(V) and is removed from the ether phase. Uranium remains in the ether.

24. Solvent extraction of the TTA complex of neptunium. A number of inner complex salts of neptunium are known, and the solubility of these salts in organic solvents under suitable conditions of acidity and concentration can be taken advantage of for analytical or purification purposes. The most widely used chelating agent is the beta diketone, α-thenoyltrifluoroacetone, (frequently referred to as TTA) which forms a strong complex with neptunium(IV) readily extractable into benzene or other non-polar solvents. High partition coefficients in favor of the organic phase are obtained in solutions sufficiently acidic (e.g. 0.5 molar H^+) that only a few other ions, notably iron(III), protactinium(V), plutonium(IV), tin(IV), zirconium(IV), cerium(IV), and hafnium(IV), are extracted. Neptunium-plutonium separations are readily effected by reducing plutonium to

plutonium(III) which is not extracted. Iodide ion in the presence of hot concentrated hydrochloric acid is often used for the reduction.

The extraction of the TTA complex of neptunium(V) and (VI) is slight.

25. Ion-exchange behavior of neptunium. The ion-exchange behavior of neptunium has not been reported in detail although ion-exchange techniques are of considerable importance. Neptunium in its three principal solution states forms negatively charged chloride complexes in strong solutions of hydrochloric acid; these complexes are readily removed from solution by exchange with anion resins such as Dowex-1 (a copolymer of styrene and divinyl benzene with quaternary ammonium functional groups). The other actinide elements show similar behavior as is shown in Table 11. The chloride concentration must be quite high for these negatively charged complexes to form; hence adsorption and desorption can be controlled by adjusting the hydrochloric acid concentration. Separation of neighboring actinide elements can be achieved by adjustment of acid concentration or by control of oxidation-reduction conditions. The separation from rare-earth contaminants is very large as these elements do not form anionic complexes in hydrochloric acid.

Table 11. Relative adsorption of actinide element ions on anion-exchange resins from strongly acidic hydrochloric acid solutions.

Hexapositive Ions	U(VI) > Np(VI) > Pu(VI) All strongly adsorbed.
Pentapositive Ions	Pa(V) and Np(V) Strongly adsorbed.
Tetrapositive Ions	Th(IV) and U(IV) Not adsorbed. Np(IV) < Pu(IV) Strongly adsorbed.
Tripositive Ions	Pu(III)-not adsorbed. Americium and higher elements-slight adsorption increasing with atomic number.

The exact change in adsorbability with hydrochloric acid concentration depends on the particular exchange resin sample. Rough data for Dowex-1 resin are the following:

Hexapositive ions. Uranium(VI), neptunium(VI), and plutonium(VI) are readily adsorbed from hydrochloric acid 6 M or greater in concentration. These ions are readily desorbed with 0 to 3 molar hydrochloric acid.

Pentapositive ions. Neptunium(V) is readily adsorbed above 4 molar hydrochloric acid. Protactinium(V) is readily adsorbed above 8 molar hydrochloric acid. Uranium(V) and plutonium(V) are not stable enough to be of radiochemical interest.

Tetrapositive ions. Uranium(IV) is adsorbed only from very concentrated hydrochloric acid. Neptunium(IV) is adsorbed above 4 molar hydrochloric acid. Plutonium(IV) is adsorbed strongly above 2.5 molar hydrochloric acid.

Anion exchange methods are attractive because they are rapid and quantitative. Neptunium can be separated from plutonium easily and quantitatively by anion exchange. If both elements are in concentrated hydrochloric acid, iodide ion can be added to reduce neptunium to the (IV) state and plutonium to the (III) state. The solution can then be drawn through a short bed of Dowex-1 resin and washed with concentrated hydrochloric acid. The plutonium passes through quantitatively while the neptunium is adsorbed quantitatively. The neptunium(IV) can then be desorbed with 0.5 molar hydrochloric acid.

Neptunium and plutonium can be separated from a large number of fission product and light element impurities by anion-exchange techniques. The greater number of those elements which form adsorbable negative ions in hydrochloric acid can be removed by procedures based on a detailed knowledge of their adsorption behavior. Kraus[19] has provided an excellent review of this field.

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[19] K. A. Kraus, Paper P/837, "Peaceful Uses of Atomic Energy Proceedings of the Geneva Conference", August 1955, United Nations.

Uranium, neptunium, and plutonium in all their stable solution oxidation states are readily adsorbed from acid solution on cation-exchange resins such as Amberlite (copolymer of formaldehyde and phenol with carboxylic and phenolic functional groups) and Dowex-50 (copolymer of styrene and divinylbenzene with nuclear sulfonic acid functional groups). Small amounts of these elements can be adsorbed on a small column of resin from rather large volumes of dilute acid solution. This property is very useful for concentration purposes. For adsorption of neptunium it is advisable to adjust the oxidation state to the tetrapositive state since the Np^{+4} ion is very much more strongly bound than is the divalent NpO_2^{+2} ion. The monovalent NpO_2^+ ion is only weakly adsorbed. On long contact with most commercial resins neptunium(VI) is reduced to lower oxidation states.

Neptunium, uranium, and plutonium ions can be desorbed from cation-exchange resin columns by elution with moderately concentrated solutions of hydrochloric acid or nitric acid as would be expected from the mass action influence of the hydrogen ion. However the elution with hydrochloric acid is much speedier, particularly for neptunium(IV), than would be expected from this effect alone because of the strong tendency toward the formation of chloride complexes. See Figure 30, Section 55.

Neptunium can be eluted from cation-exchange resin columns with other eluting agents which form complex ions with neptunium. Data on such elution behavior is scanty.

II. PLUTONIUM (ELEMENT 94)

a. History of Plutonium

26. Discovery of plutonium--summary of known isotopes. McMillan and Abelson[20] found that Np^{239}, formed by the beta decay of U^{239}, underwent radioactive decay by the emission of beta particles. They were unable to detect the Pu^{239} in their samples because of the long half life of this isotope. The first isotope of element 94 to be identified was Pu^{238} produced in the experiments of Seaborg, McMillan, Wahl, and Kennedy[21] by the bombardment of uranium by 14-Mev deuterons in the University of California cyclotron.

$$U^{238}(d,2n)Np^{238} \xrightarrow[2.1\ \text{days}]{\beta^-} Pu^{238} \qquad (26.1)$$

The isotope Pu^{238} was shown to emit alpha particles with a half life of approximately 50 years (best present value = 90 years). The discoverers proposed the name plutonium (symbol Pu) from Pluto, at that time believed to be the second planet beyond Uranus in our solar system.

In 1941, Kennedy, Seaborg, Segrè, and Wahl[22] isolated and identified Pu^{239} as the decay product of a very intense source of Np^{239}. This isotope Pu^{239} decays by the emission of alpha particles, with the half life (best value determined later) of 24,360 years. These same investigators demonstrated that Pu^{239} underwent nuclear fission with a high cross section when bombarded with slow neutrons.[23] Because of this high cross section (730×10^{-24} cm^2) and because it can be prepared in kilogram quantities in nuclear reactors it is of very considerable importance in nuclear weapons and in the controlled release of nuclear power in reactors.

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[20] E. M. McMillan and P. Abelson, Phys. Rev. 57, 1185 (1940).

[21] G. T. Seaborg, E. M. McMillan, J. W. Kennedy, and A. C. Wahl, Phys. Rev. 69, 366 (1946); G. T. Seaborg, A. C. Wahl, and J. W. Kennedy, ibid. 69, 367 (1946).

[22] J. W. Kennedy, G. T. Seaborg, E. Segrè, and A. C. Wahl, Phys. Rev. 70, 555 (1946).

[23] J. W. Kennedy, G. T. Seaborg, E. Segrè, and A. C. Wahl, Report A-33, May 29, 1941.

In a chain-reacting pile, plutonium is produced via the reactor sequence

$$U^{238}(n,\gamma)U^{239};\ U^{239} \xrightarrow[23\ \text{min}]{\beta^-} Np^{239} \xrightarrow[2.33\ \text{days}]{\beta^-} Pu^{239}. \qquad (26.2)$$

The first isolation of a weighable amount of plutonium free from all carrier matter and impurities was carried out by Cunningham and Werner[24] in 1942.

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[24] B. B. Cunningham and L. B. Werner, paper 1.8, N.N.E.S. Vol. 14B, "The Transuranium Elements," 1949.

Minute amounts of plutonium were found in pitchblende by Seaborg and Perlman[24a] and in a series of uranium and thorium ores by Levine and Seaborg.[24b] The ratio of plutonium to uranium in pitchblende and monazite ores is approximately 10^{-11} and substantially less in carnotite and fergusonite. All the plutonium isolated was Pu^{239} formed from the uranium by the reaction (26.2). The sources of the neutrons include (1) the spontaneous fission of uranium, (2) (α,n) reactions caused by the action of alpha particles from the heavy elements on the nuclei of light elements in the ore, and (3) cosmic rays. In the case of pitchblende ores, the spontaneous fission of uranium and (α,n) reactions contribute the major portion of the neutrons. In thorium ores, neutrons from (α,n) reactions are probably dominant. Peppard and coworkers[24c] isolated microgram quantities of plutonium from Belgian Congo pitchblende concentrates. They examined this plutonium carefully for higher mass plutonium isotopes by neutron irradiation techniques and by mass spectroscopy and proved that it was pure Pu^{239}.

[24a] G. T. Seaborg and M. L. Perlman, paper 1.3, N.N.E.S. Vol. 14B, "The Transuranium Elements"; J. Am. Chem. Soc. 70, 1571 (1948).

[24b] C. A. Levine and G. T. Seaborg, J. Am. Chem. Soc. 73, 3278 (1951).

[24c] D. F. Peppard et al., J. Am. Chem. Soc. 73, 2529 (1951).

Table 12 lists all known isotopes of plutonium together with their principal decay characteristics. Figure 11 shows detailed decay schemes for the more carefully studied isotopes. Nuclear data for the transuranium elements as a group is summarized in Section C at the end of this article. The lighter isotopes are produced by bombardment of uranium with high energy helium ions while the heavier isotopes are produced by multiple neutron capture reactions in high flux reactors starting with plutonium isotopes of lower mass.

Figure 11. Decay schemes of plutonium isotopes.

Table 12. Isotopes of Plutonium*

Isotope and Half Life	Type of Decay	Energy (Mev)	Method of Production	Disintegration Energies (Mev)†
Pu^{232}	EC < 98%		U^{235}(α,7n)	$Q_{EC} = 0.99$
36 m	α > 2%	6.58	U^{233}(α,5n)	$Q_{\alpha} = 6.70$ est.
Pu^{234}	EC 96%		U^{235}(α,5n)	$Q_{EC} = 0.48$ calc.
9.0 h	α 4%	6.19	U^{233}(α,3n)	
	No γ < 0.5% (Ref. 1)		daughter Cm^{238}	$Q_{\alpha} = 6.30$
Pu^{235}	EC 99+ %		U^{233}(α,2n)	$Q_{EC} = 1.17$ calc.
26 m	α 0.002 %		U^{235}(α,4n)	$Q_{\alpha} = 5.95$
Pu^{236}	α	5.75	U^{233}(α,n)	$Q_{\alpha} = 5.85$
2.7 y α	β stable		U^{235}(α,3n)	
3.5 x 10^{9} y spon. fission	γ	0.045	U^{238}(α,6n) Np^{237}(d,3n) daughter Cm^{240}	
Pu^{237}	EC		Np^{237}(p,n)	$Q_{EC} = 0.18$ est.
40 d	γ	0.064	U^{235}(α,2n)	$Q_{\alpha} = 5.72$ est.
	X rays		Np^{237}(d,2n)	
Pu^{238}	α	5.352 (0.09%) 5.452 (28%)	U^{238}(d,2n)	$Q_{\alpha} = 5.59$
89.6 y α	β stable	5.495 (72%) (Ref. 2)	U^{238}(α,4n)	
4.9 x 10^{10} y spon. fission	γ	0.0438, 0.099 (Ref. 2)	U^{235}(α,n)	
	X ray	0.150 (Ref. 2) 0.203 (Ref. 8)	daughter Np^{238} daughter Cm^{242}	
Pu^{239}	α	5.150 (69%) 5.137 (20%)	U^{238}(α,3n)	$Q_{\alpha} = 5.24$
24,360 y	β stable	5.099 (11%)	Pu^{238}(n,γ)	I = 1/2
5.5 x 10^{15} y spon. fission	γ	0.039, 0.0531, 0.100, 0.124, 0.384	daughter Np^{239}	

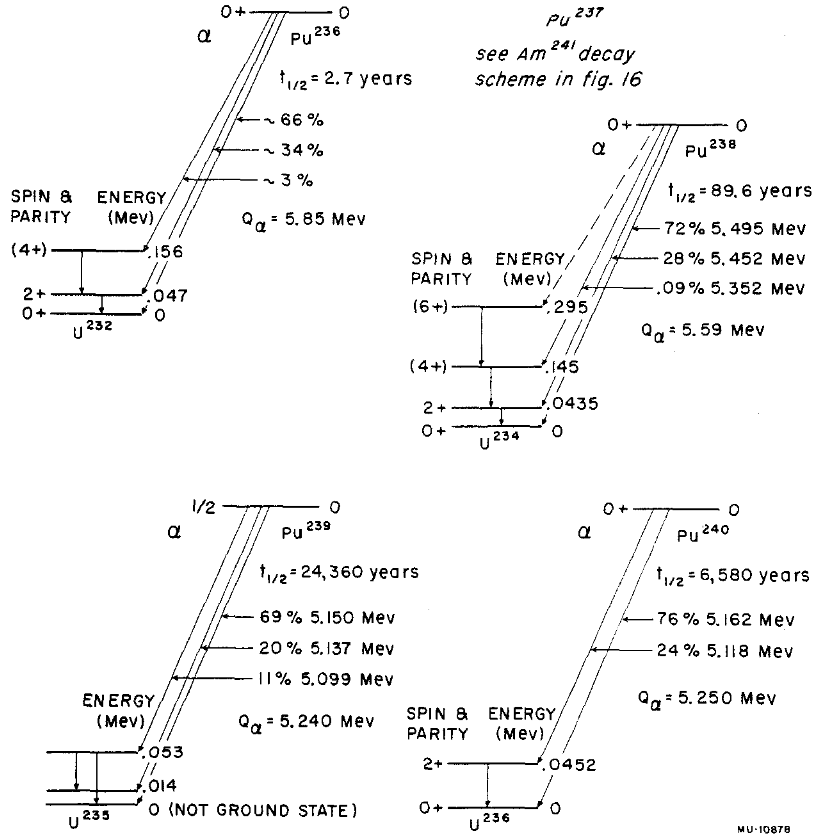

0+
0
α
Pu236
t1/2 = 2.7 years
~66 %
~34 %
~3 %
SPIN & PARITY
ENERGY (Mev)
Qα = 5.85 Mev
(4+)
.156
2+
.047
0+
0
U232
Pu237
see Am241 decay scheme in fig. 16
0+
0
α
Pu238
t1/2 = 89.6 years
72 % 5.495 Mev
28 % 5.452 Mev
.09 % 5.352 Mev
SPIN & PARITY
ENERGY (Mev)
Qα = 5.59 Mev
(6+)
.295
(4+)
.145
2+
.0435
0+
0
U234
1/2
0
α
Pu239
t1/2 = 24,360 years
69 % 5.150 Mev
20 % 5.137 Mev
11 % 5.099 Mev
ENERGY (Mev)
Qα = 5.240 Mev
.053
.014
0 (NOT GROUND STATE)
U235
0+
0
α
Pu240
t1/2 = 6,580 years
76 % 5.162 Mev
24 % 5.118 Mev
Qα = 5.250 Mev
SPIN & PARITY
ENERGY (Mev)
2+
.0452
0+
0
U236
MU-10878

Figure 11

Table 12 (Continued)

Isotope and Half Life	Type of Decay	Energy (Mev)	Method of Production	Disintegration Energies (Mev)
Pu^{240}	α	5.162 (76%) 5.118 (24%)	$Pu^{239}(n,\gamma)$	$Q_{\alpha} = 5.25$
6580 y α	β stable		U^{238} $(\alpha,2n)$	
1.2×10^{11} y spon. fission	γ	0.0452		
Pu^{241}	β^-	0.021	$Pu^{240}(n,\gamma)$	$Q_{\beta} = 0.02$
13.0 y	α 10^{-3}%	4.91	$U^{238}(\alpha,n)$	$Q_{\alpha} = 5.13$
(Ref. 3)	γ	0.100, 0.145		I = 5/2
Pu^{242}	α	4.898	$Pu^{241}(n,\gamma)$	
3.9×10^5 y (Ref. 4) 3.78×10^5 y (Ref. 10) 7.3×10^{10} y spon. fission	β stable		daughter Am^{241m}	$Q_{\alpha} = 4.98$
Pu^{243}	β^-	0.37 (12%), 0.468 (35%)	$Pu^{242}(n,\gamma)$	$Q_{\beta} = 0.56$
4.98 h		0.57(53%) (Ref. 5)		$Q_{\alpha} = 4.71$ calc.
	γ	0.085, 0.12 (Ref. 5)		
Pu^{244} 7×10^7 y α (Ref. 6) 2.5×10^{10} y spon. fission	α(Ref. 6)		$Pu^{243}(n,\gamma)$ (Ref. 6)	$Q_{\alpha} = 4.57$ est.
Pu^{245}	β^-		$Pu^{244}(n,\gamma)$	$Q_{\beta} = 1.31$ est.
10.1 h (Ref. 7, 8, 9)				$Q_{\alpha} = 4.44$ est.
Pu^{246}	β^-(Ref. 7)			
11.2 d (Ref. 7)	γ	0.043, 0.103, 0.175, 0.220 (Ref. 7)	$Pu^{245}(n,\gamma)$ (Ref. 7)	$Q_{\alpha} = 4.30$ est. $Q_{\beta} = 0.37$

Table 12 (Continued)

*For references to original data not given specifically here, refer to Hollander, Perlman, and Seaborg, "Table of Isotopes," Revs. Modern Physics 25, 469 (1953) and to the compilations of the Nuclear Data Group, National Research Council.

† Revised values taken from Glass, Thompson, and Seaborg, J. Inorg. Nucl. Chem., 1, 3 (1955).

[1] R. W. Hoff, Ph.D. Thesis, University of California Radiation Laboratory Report UCRL-2325 (September 1953).

[2] F. Asaro and I. Perlman, Phys. Rev. 94, 381 (1954).

[3] D. R. MacKenzie *et al.*, Phys. Rev. 90, 327 (1953).

[4] F. Asaro and I. Perlman, Revs. Modern Physics 26, 456 (1954).

[5] D. W. Engelkemeir *et al.*, Phys. Rev. 90, 6 (1953).

[6] W. C. Bentley *et al.*, Paper P/809, "Proceedings of the Geneva Conference--Peaceful Uses of Atomic Energy," August 1955, United Nations.

[7] D. W. Engelkemeir *et al.*, J. Inorg. Nucl. Chem. 1, 345 (1955).

[8] C. I. Browne *et al.*, J. Inorg. Nucl. Chem. 1, 254 (1955).

[9] M. H. Studier *et al.*, J. Inorg. Nucl. Chem. 1, 262 (1955).

[10] J. Mech *et al.*, Argonne National Laboratory Report ANL-5348 (1954).

b. The Chemical Properties of Plutonium

27. Solution oxidation states. In aqueous solution plutonium exhibits the four oxidation states (III), (IV), (V), and (VI) so that its chemical reactions are quite complex. In acidic solution the ion species corresponding to these oxidation states are Pu^{+3}, Pu^{+4}, PuO_2^{+}, and PuO_2^{+2}. Each ion is hydrated, but no exact information on the hydration is available. The aqueous ions have characteristics colors: Pu^{+3} (blue-lavender), Pu^{+4} (yellow-brown), and PuO_2^{++} (pink orange). Pure solutions of PuO_2^{+} have not been prepared and since the ion shows but little absorption of visible light, its appearance in solution is not definitely known; presumably dilute solutions would be colorless and concentrated solutions of PuO_2^{+} would have a reddish appearance since the ion absorbs mainly in the shorter and medium wave lengths of the visible spectrum. The colors of the plutonium ions are altered by hydrolysis or complex ion formation.

The formal oxidation potential scheme for plutonium in 1 molar perchloric acid is given in Figure 12.

Figure 12. Formal Oxidation Potential Diagram of Plutonium in Perchloric Acid

$$\begin{tikzcd}
Pu^{0} \arrow[r, "+2.03"] & Pu^{+3} \arrow[r, "-0.982"] & Pu^{+4} \arrow[r, "-1.161"] \arrow[rr, dash, bend right, "-1.043"'] & PuO_2^{+} \arrow[r, "-0.925"] & PuO_2^{+2}
\end{tikzcd}$$

The potentials of Figure 12 are applicable in dilute hydrochloric acid or nitric acid systems with but slight changes because the chloride and nitrate complexes are relatively weak. In stronger complexing media such as sulfate, phosphate, fluoride, or oxalate solutions or in solutions containing organic chelating agents considerable complexing of plutonium occurs. The tendency of the ions to form complexes increases in the order $PuO_2^{+} < Pu^{+3} < PuO_2^{+2} < Pu^{+4}$ and the observed potential changes are in the direction expected from this.

Oxidation-reduction interconversions of the Pu^{+3}-Pu^{+4} pair or of the PuO_2^+ - PuO_2^{+2} pair are rapid and readily reversible because only electron transfer is involved. When Pu^{+4} is converted to PuO_2^+ or PuO_2^{+2}, however, chemical bonds must be changed and such reactions may be slow. An interesting part of plutonium chemistry is a study of the reaction kinetics and mechanisms of oxidation-reduction reactions.

28. Equilibria involving the plutonium aqueous ion species. Plutonium chemistry takes on an additional complexity from the fact that the oxidation potentials connecting the (III), (IV), (V), and (VI) states are so close in value to each other. This means that appreciable concentrations of several oxidation states can exist at equilibrium in the same solution and that pure solutions of intermediate oxidation states undergo disproportionation (self oxidation and reduction reactions).

Disproportionation of plutonium(IV) can be written

$$3Pu^{+4} + 2H_2O \rightleftharpoons PuO_2^{+2} + 2Pu^{+3} + 4H^+. \qquad (28.1)$$

The reverse reaction is called reproportionation. The equilibrium quotient, K_1, for disproportionation is:

$$K_1 = \frac{[PuO_2^{+2}][Pu^{+3}]^2[H^+]^4}{[Pu^{+4}]^3} \qquad (28.2)$$

From the potentials of figure 12, K_1 for perchloric acid solutions at room temperature is calculated to be 0.0086. A pure solution of plutonium(IV) would disproportionate in 0.5 molar acid to give a solution consisting of 50.6 percent plutonium(IV), 33 percent plutonium(III), and 16.5 percent plutonium(VI). In 1.0 molar acid the final concentrations would be 72 percent plutonium(IV), 18.6 percent plutonium(III), and 9.3 percent plutonium(VI). The value of K_1 is much greater at elevated temperatures e.g. ~ 3.3 in 0.95 molar hydrochloric acid at 70° C. Disproportionation is greatly suppressed in solutions containing complexing agents because of the greater stabilization of plutonium(IV). The rate of disproportionation is slow at room temperature. For example, 1.93×10^{-3} molar plutonium(IV) in 0.5 molar hydrochloric acid at 25° C does not come to equilibrium with plutonium(III) and plutonium(VI) for about 100 hours. Equilibrium is much more rapid in more concentrated solutions and at elevated temperatures.

Another equilibrium of considerable importance is represented by the equation

$$PuO_2^+ + Pu^{+4} \rightleftharpoons PuO_2^{+2} + Pu^{+3}. \qquad (28.3)$$

This equilibrium is unimportant in strongly acidic media because PuO_2^+ is relatively unstable with respect to the other oxidation states and can exist to the extent of less than one or two percent at equilibrium. In solutions of lower acidity e.g. < 0.2 molar it is necessary to consider all four plutonium ion species.

The oxidation potentials can be used to calculate the value of the equilibrium quotient:

$$K_2 = \frac{[Pu^{+3}][PuO_2^{+2}]}{[Pu^{+4}][PuO_2^+]} = 9.2 \qquad (28.4)$$

Values of this constant have been determined in a number of solutions. This equilibrium shows no acid dependence and since the reaction involves only an electron transfer, equilibrium is rapidly attained. Since the disproportionation reaction previously discussed goes at a slow rate the very striking situation is possible in which four oxidation states of the element are in balance with respect to each other at the same time that three of the oxidation states are out of balance with respect to one another.

Another reaction between plutonium ions which can be written is

$$3PuO_2^+ + 4H^+ \longrightarrow 2PuO_2^{+2} + Pu^{+3} + 2H_2O. \qquad (28.5)$$

This is known as the disproportionation of plutonium(V). In the pH region just below pH 1.4 where the concentration of Pu^{+4} is greatly reduced this equilibrium is the principal equilibrium involving the plutonium ions. When the acidity is reduced below pH 1.4 plutonium(IV) becomes stabilized by hydrolysis and plutonium(V) rapidly becomes less important. In strongly acidic solutions the equilibrium concentration of PuO_2^+ is quite small because of the fourth power acid dependence. Nevertheless reaction (28.5) is still of importance in strongly acid solutions because of the role it plays in the mechanism of many oxidation-reduction reactions.

The equilibrium quotient

$$K_3 = \frac{[PuO_2^{+2}]^2[Pu^{+3}]}{[PuO_2^+]^3[H^+]^4}$$

is calculated to be 8.9×10^9 in perchloric acid from the potentials of Figure 12.

The equilibrium quotients for all three reactions discussed in this section are markedly affected by complexing agents such as sulfate, phosphate, oxalate, etc. It is also true that ion concentrations in plutonium solutions may not stabilize at the values predicted by the equilibrium quotients given in this section because of the reducing effect of the alpha radiation of the plutonium. The alpha radiation, particularly in moderately concentrated solutions, causes a slow lowering of the overall oxidation state of the plutonium in solution.

29. Absorption spectra of plutonium ions. Figure 13 shows the absorption spectra of the aqueous ions of plutonium. The curves for plutonium(III), (IV), and (V) represent measurements taken in 0.5 M hydrochloric acid, that for plutonium(VI) in 0.5 M nitric acid, and that for colloidal plutonium(IV) in 0.15 M hydrochloric acid. Essentially identical spectra are observed in perchloric acid solutions or other media where complexing is slight. The sharp absorption bands are attributed to electronic transitions within the 5f shell, preserving the configuration $5f^n$ in upper and lower states as was discussed previously. The distinct peaks characteristic of the individual oxidation states are widely employed in the analysis of plutonium solutions to determine the amount of each oxidation state present.

Figure 13. Summary of absorption spectra of aqueous ions of plutonium in its various oxidation states.

Reproduced from R. E. Connick et al., N. N. E. S. Vol. 14B, "The Transuranium Elements", paper 4.20, p. 588.

The principal absorption peaks are listed in Table 13.

Table 13. Wave lengths of absorption bands characteristic of plutonium oxidation states (millimicrons).

Pu^{+3}	5620	6025	6660	7500	8500	9500
Pu^{+4}	4700	6650	7000	7300	8150	
PuO_2^+	5690	7750				
PuO_2^{+2}	8330	9530	9830			

30. Hydrolysis of plutonium ions. Plutonium(III) does not undergo appreciable hydrolysis below pH 7. In strongly alkaline solution it is completely precipitated as $Pu(OH)_3$, the solubility product being approximately 2×10^{-20}. In moist air $Pu(OH)_3$ is oxidized to $Pu(OH)_4$. The formal oxidation potential is +0.95 volts for the reaction

$$Pu(OH)_3 + OH^-_{aq.} \longrightarrow Pu(OH)_4 + e^- . \qquad (30.1)$$

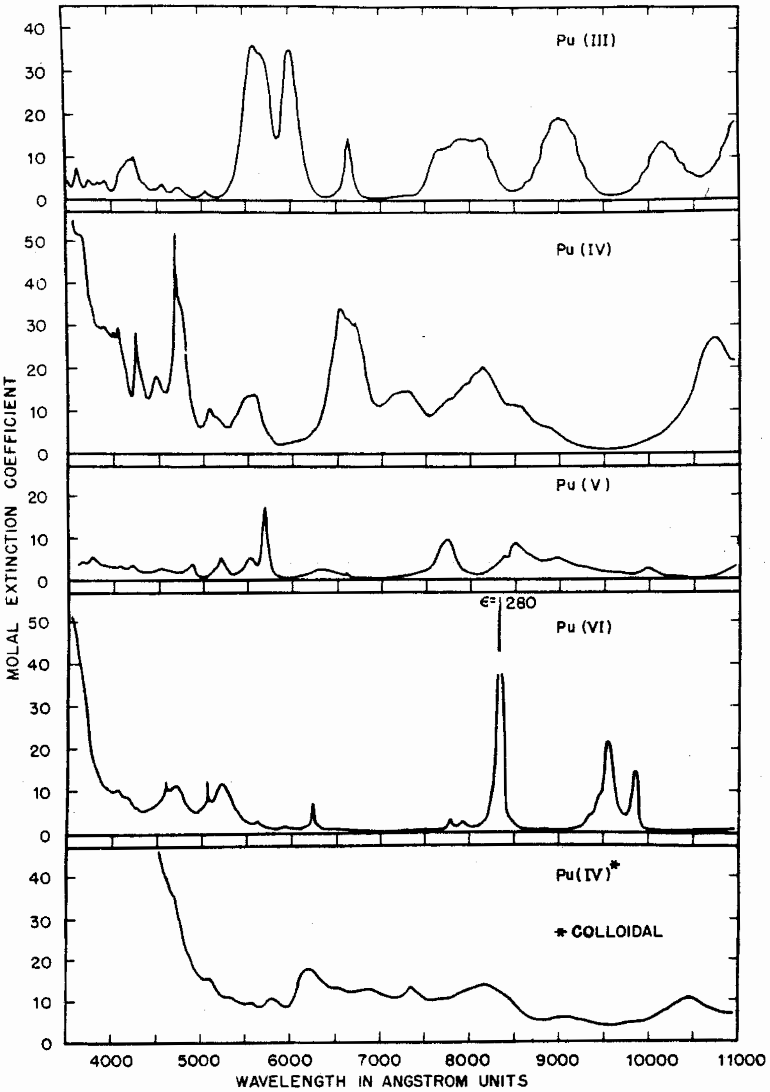
The green hydroxide of tetrapositive plutonium is noted for its extreme insolubility. The solubility product $K_{SP} = [Pu^{+4}][OH^-]^4$ is estimated to be 7×10^{-56}. The hydroxide begins to form at 0.1 molar hydrogen ion concentration for 0.001 M plutonium(IV).

One rather unusual property of tetrapositive plutonium is a tendency to polymerize into a very stable green-colored colloid in solutions of low acidity ($pH > 1$). The polymeric or colloidal plutonium(IV) is in the form of cationic aggregates of the hydroxide or hydrous oxide consisting of particles of high molecular weight, probably of the order of tens of millions, with a small overall positive charge. In the pH range 1 - 3 the polymer is suspended as a dispersed colloid. At higher pH, particularly above pH 5, it coagulates readily to a green precipitate. Dissolution of the polymer in acid solution may be quite slow.

There is little evidence for the hydrolysis of PuO_2^+ in basic solutions below pH 9. The hydroxide $PuO_2(OH)$ is quite soluble.

A solid hydroxide of plutonium(VI) has not been identified but plutonyl ion binds two hydroxide groups near pH 5.5. $PuO_2(OH)_2$ is the main species in neutral solution. A third hydroxide is added near pH 9 or 10 to form a plutonate ion which may undergo polymerization. In the presence of such cations as magnesium or calcium at high pH moderately-insoluble plutonate salts precipitate from solution.

The hydrolytic behavior of the plutonium ions is not known quantitatively so that no reliable oxidation potential scheme can be quoted for alkaline solutions. Connick has proposed the scheme shown in Figure 14 for 1 molar hydroxide solutions.



MU-10960

Figure 13

Figure 14. Formal potential scheme for plutonium in 1 molar hydroxide.*

$$\begin{tikzcd}
\underset{\text{solid}}{Pu(OH)_3\cdot xH_2O} \arrow[r, "+0.95"] & \underset{\text{solid}}{Pu(OH)_4\cdot yH_2O} \arrow[r, "-0.76"] \arrow[rr, dash, bend right, "\sim -0.4"'] & PuO_2(OH)_{aq.} \arrow[r, "-0.26"] & PuO_2(OH)_3^-\ aq.
\end{tikzcd}$$

* R. E. Connick, Chapter 8, N.N.E.S. Vol. 14A, "The Actinide Elements," 1952.

31. Stability of plutonium(V). It has been noted in previous discussion that neptunium(V) is stable in acid solutions of moderate strength, while plutonium(V) because of the disproportionation reaction (28.5) is of little importance above 0.5 molar acidity. This is an important difference in the chemistry of the two elements. The optimum acidity range for the existence of plutonium(V) is pH 2 to 7. Gevantman and Kraus[25] noted that a pure 0.0007 molar solution of PuO_2^+ was less than ten percent disproportionated in 350 hours at pH 3.52. Increase of temperature and of plutonium concentration increase the extent of disproportionation. It is doubtful whether PuO_2^+ is thermodynamically stable at any pH but the uncertainties in the hydrolysis of plutonium(IV) and the free energy of formation of plutonium(IV) polymer make it hard to settle this point with certainty.

32. Oxidation reduction behavior of plutonium. In tracer solutions the mechanism of oxidation or reduction reactions must involve the direct action of the oxidizing or reducing agent on the plutonium ions. Such reactions may be slow when conversion of oxygenated to unoxygenated ions is involved even though the oxidation potential of the solution is favorable to the reaction. In moderately concentrated solutions of plutonium the mechanism of reaction may involve the disproportionation of plutonium(IV) or of plutonium(V). When disproportionation is the rate determining step, oxidation-reduction reactions can be speeded up by adjustment of conditions to favor disproportionation.

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[25] L. H. Gevantman and K. A. Kraus, paper 4.16, N.N.E.S. Vol. 14B, "The Transuranium Elements," 1949.

In this section the behavior of plutonium when treated with common reducing and oxidizing agents will be summarized. Most statements refer to behavior at room temperature.

Oxidation of plutonium(III) to plutonium(IV) occurs rapidly with bismuthate ion, bromate ion, iron(III), cerium(IV), dichromate ion, iodate ion, permanganate ion, etc. Oxidation by dilute nitric acid is slow at room temperature; the reaction mechanism involves nitrous acid or the oxides of nitrogen so that the addition of reagents which rapidly destroy nitrous acid will stabilize plutonium(III) in nitric acid. Prevention of the oxidation of plutonium beyond plutonium(IV) is aided by the addition of complexing agents such as sulfate or concentrated nitric acid.

Rapid or relatively rapid reduction of plutonium(IV) to plutonium(III) occurs with ferrous ion, hydroquinone, iodide ion, nitrous acid, hydroxylamine, hydrazine, sulfurous acid, and zinc metal.

Plutonium(IV) is oxidized slowly to higher oxidation states by bromate ion, dichromate ion, permangante ion, and nitrate ion. Oxidation by bismuthate ion, ceric ion, argentic ion, or by peroxydisulfate ion in the presence of silver ion is rapid.

Reduction of plutonium(VI) to plutonium(V) by iodide ion is very rapid but at room temperature further reduction is slow. Reduction of plutonium(VI) at pH 1.2 by iodide ion is a good method for the preparation of nearly pure plutonium(V) solutions. Ferrous ion reduces plutonium(VI) rapidly to plutonium(IV) or (III). Ferrous ion may be used in combination with other reducing agents to catalyze reduction below the pentapositive state. Hydrogen peroxide reduces plutonium(VI) to plutonium(V) at a rather rapid rate. Further reduction appears to proceed by the disproportionation mechanism. Hydrogen gas in the presence of platinized platinium will reduce plutonium(VI) to plutonium(V) and ultimately to lower oxidation states. Hydroxylamine, hydrazine, sulfurous acid, and other reducing agents reduce plutonium(VI) at a moderate but measurable rate to plutonium(V) at room temperature. Further reduction occurs slowly via the disproportionation of plutonium(V).

33. Compounds of plutonium.[26] Plutonium metal has astonishing properties.[27,28,29] It exists in five allotropic forms below its melting point (637° C) at atmospheric pressure, a behavior unique to this metal. The temperatures at which the phase changes occur are given in Table 14. Severe temperature hysteresis effects are observed so different values are given for heating and cooling.

Table 14. Phase Transitions in Plutonium Metal[27]

Phase Change	Temperature of Transition (°C)	
	Heating Cycle	Cooling Cycle
$\alpha \rightleftharpoons \beta$	136	85
$\beta \rightleftharpoons \gamma$	225	about 160
$\gamma \rightleftharpoons \delta$	320	about 250
$\delta \rightleftharpoons \epsilon$	480	about 480
$\epsilon \rightleftharpoons$ liquid	637 ± 5°C	

The density of α-plutonium is quite high, 19.2. The densities of the other phases are markedly lower, namely 17.3 for β-plutonium, 16.7 for δ-plutonium, and 16.3 for ε-plutonium. Marked changes in electrical resistivity and thermal expansion also occur. The electrical resistivity of α-plutonium has the value 150 micro-ohm centimeters, higher than any other "metallic" element at room temperature. Plutonium metal is highly electropositive.

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[26] A detailed review of the compounds of plutonium is given by B. B. Cunningham, Chapter 10, N.N.E.S. Vol. 14A, "The Actinide Elements," 1954.

[27] C. S. Smith, Phys. Rev. 94, 1068 (1954).

[28] W. B. H. Lord, Nature 173, 534 (1954).

[29] J. A. L. Robertson et al., Nature 173, 535 (1954).

The principal plutonium halides and oxyhalides are summarized in Table 15.

Table 15. Halides and oxyhalides of plutonium.[1,2]

Compound	Color	Crystal Structure	Density	M.P. (°C)	ΔH Formation (Kcal per mole)[3]
PuF_6	deep brown gas red or reddish brown solid	orthorhombic	-	50.75	-
PuF_4	light brown	monoclinic	7.0	-	-424
PuF_3	violet	hexagonal, tysonite type	9.32	1425	-375
$PuCl_3$	emerald green	hexagonal, UCl_3 type	5.70	760	-230
$PuBr_3$	green	orthorhombic	6.69	681	-198.8
PuI_3	bright green	orthorhombic	6.92	770 est.	-155
PuOF	metallic	tetragonal	9.76	above 1635	-
PuOCl	blue green	tetragonal PbFCl type	8.81	-	-223.6
PuOBr	deep green	tetragonal PbFCl type	9.07	-	-210
PuOI	green	tetragonal PbFCl type	8.46	-	-190

[1] Crystal data from W. H. Zachariasen, paper 20.6, N.N.E.S. Vol 14B, "The Transuranium Elements," 1949.

[2] Lattice constants are given in table 6, section 6.

[3] Heat of formation data from B. B. Cunningham, chapter 10, N.N.E.S. Vol 14A, "The Actinide Elements," 1952.

The very insoluble plutonium trifluoride is precipitated from acid solutions containing hydrofluoric acid. The crystalline anhydrous compound is readily prepared by treating PuO_2, PuF_4, $PuO_2 \cdot xH_2O$, $Pu(NO_3)_4 \cdot xH_2O$, or $Pu(C_2O_4)_2 \cdot xH_2O$ with anhydrous hydrogen fluoride - hydrogen mixtures at 500 - 600° C.

Plutonium tetrafluoride is very insoluble and is precipitated in hydrated form with hydrofluoric acid. Anhydrous crystalline PuF_4 is prepared by treatment of plutonium dioxide or oxalate with hydrogen fluoride gas plus oxygen at 550 - 600° C.

Plutonium hexafluoride, the volatile plutonium analogue of uranium hexafluoride, can be made by the reaction of pure gaseous fluorine on plutonium tetrafluoride at 700° C. Successful preparation of the compound depends on the instant condensation of the compound on a cooled surface located close to the reaction zone.[30] The melting point of the hexafluoride is 50.75° C; it is by far the most volatile compound of plutonium. It is thermodynamically unstable with respect to dissociation into fluorine and plutonium tetrafluoride and is a powerful fluorinating agent. The rate of decomposition when stored as a vapor is, however, only about 0.1 percent per day. When it is stored principally as a solid, the radiation decomposition induced by the intense alpha activity destroys about 1.5 percent of the hexafluoride per day. Plutonium hexafluoride is isostructural with uranium and neptunium hexafluoride.

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[30] J. G. Malm and B. Weinstock, Paper P/733, "Proceedings of the Geneva Conference--Peaceful Uses of Atomic Energy," August 1955, United Nations. Additional information on PuF_6 will appear in papers by A. E. Florin, I. R. Tannenbaum, and J. F. Lemons, Los Alamos Scientific Laboratory; R. Hurst and collaborators, Harwell Atomic Energy Establishment; N. J. Hawkins, H. C. Mattraw, and W. W. Sabol, Knolls Atomic Power Laboratory.

A number of plutonium double fluorides such as $NaPuF_4$, $NaPuF_5$, $KPuF_5$, NH_4PuF_5, KPu_2F_9, and $CsPu_2F_2$ have been precipitated from aqueous solution and analyzed crystallographically. These double salts are more insoluble than the simple plutonium fluorides.

The compound $PuO_2F_2 \cdot xH_2O$ is very soluble although double salts such as $RbPuO_2F_3$ are somewhat less soluble.

Anhydrous plutonium trichloride may be prepared by the action of various strong chlorinating agents on plutonium dioxide at elevated temperatures or by the direct burning of plutonium metal in chlorine at 450° C. The trichloride sublimes at 800° C. The anhydrous compound is hygroscopic. A well defined monohydrate, trihydrate, and hexahydrate of plutonium are known.

Anhydrous plutonium tetrachloride is not stable and has not been prepared, a distinction from neptunium tetrachloride or uranium tetrachloride.

Anhydrous crystalline plutonium tribromide may be prepared by the action of anhydrous hydrogen bromide gas on plutonium dioxide or oxalate at elevated temperature or by direct burning of the metal in bromine at 300 - 325° C. At 750 - 800° C the tribromide is appreciably volatile and may be purified by sublimation in a vacuum. The tribromide is very soluble in water. Plutonium tetrabromide is apparently not stable at any temperature.

Anhydrous plutonium triiodide may be prepared by the action of anhydrous hydrogen iodide gas on plutonium metal at 450° C. Only the oxyiodide is produced by the reaction of hydrogen iodide with the dioxide.

Plutonium oxyfluoride (PuOF), plutonium oxychloride (PuOCl), and plutonium oxyiodide (PuOI) are well characterized anhydrous compounds.

The principal oxide of plutonium is plutonium dioxide, PuO_2. It is obtained by ignition of the "hydroxide," peroxide, oxalate, sulfate or nitrate of plutonium(IV), the oxalate of plutonium(III), or the nitrate of plutonium(VI) in air or oxygen within the temperature range 500 - 1000° C. Plutonium dioxide crystallizes in a well defined face-centered cubic structure. It is a suitable compound for weighing in gravimetric analysis. The calculated density is 11.44. Oxidation to a higher oxide has not been achieved. No oxide similar to the well known uranium oxides, U_3O_8 or UO_3, have been prepared. Plutonium dioxide which has been strongly ignited is extremely difficult to dissolve.

Partially reduced oxides in the composition range Pu_2O_3 - Pu_4O_7 have been made by ignition of PuO_2 in vacuo at very high temperatures.

Plutonium monoxide, PuO, has been obtained by the reduction of PuOCl with barium vapor at 1250° C. It may appear on the surface of metal exposed to air. It is semi-metallic in character.

Plutonium(IV) peroxide is formed when hydrogen peroxide is added to acid solutions of plutonium in any oxidation state, particularly in the presence of sulfate ion. The compound is very insoluble and is a convenient choice for the direct precipitation of plutonium. This precipitation effects a high degree of purification from most light elements, cationic impurities and from most heavy elements except zirconium, thorium, and uranium. It is not suitable for gravimetric determination. The peroxide is readily dissolved in strong nitric acid and is catalytically decomposed by ferric ion.

The *hydroxides of plutonium* were discussed in the previous section on hydrolysis.

Other compounds of plutonium(III) or plutonium(IV) with very low to small solubility in acid solution include *plutonium(III) phosphate*, *plutonium(IV) dimonohydrogen phosphate*, *plutonium(IV) diphenylarsonate*, *diplutonium(III) trioxalate*, and *plutonium(IV) dioxalate*.

One of the most important compounds of hexapositive plutonium is *sodium plutonyl acetate*, $NaPuO_2(C_2H_3O_2)_3$. This pink compound is isostructural with the analogous compounds of uranium, neptunium, and americium.

Carbides, nitrides, silicides, and *sulfides*. Plutonium forms several binary compounds which are of interest because of their refractory character. The properties of these compounds are given in table 16.

Table 16. Some Binary Compounds of Plutonium.

Compound	Color and Appearance	Crystal Structure[1,2,3]	Density[4] (g/cc)	Approx. Temp. Limit for Stability in High Vacuum (°C)
PuC	black, semimetallic	cubic, rock salt type	13.99	2000
PuN	brown	cubic, rock salt type	14.22	1500
α-$PuSi_2$	silverly, metallic	tetragonal, $ThSi_2$ type	9.12	1000
β-$PuSi_2$[5]	-	hexagonal β-USi_2 type	9.18	-
$PuS_{1.33-1.5}$	black	cubic, Ce_3S_4 type	8.14	1200

[1] W. H. Zachariasen, Paper 20.2, N.N.E.S. Vol. 14B, "The Transuranium Elements," 1949.

[2] Ibid., paper 20.3.

[3] Ibid., paper 20.4.

[4] Calculated from x-ray data.

[5] O. J. C. Runnalls and R. R. Boucher, Acta. Cryst. 8, 592 (1955).

The monocarbide is formed by reacting the dioxide in intimate mixture with carbon at about 1600° C, and the mononitride may be obtained by heating the trichloride in a stream of anhydrous ammonia at 900° C; it is prepared more easily, however, by reacting finely divided metal with ammonia at 650° C. Although the lower temperatures are favorable to the production of higher nitrides, none are obtained, in contrast to the uranium-nitrogen system in which compositions up to $UN_{1.75}$ are easily realized.

The disilicide is formed when a slight stoichiometric excess of calcium disilicide is heated with plutonium dioxide in vacuum at about 1550° C. The disilicide is only moderately stable in air and burns slowly to the dioxide when heated to about 700° C.

Plutonium "sesquisulfide" may be prepared by prolonged treatment of the dioxide in a graphite crucible with anhydrous hydrogen sulfide at 1340 - 1400° C, or by reaction of the trichloride with hydrogen sulfide at 900° C.

The most important compounds of plutonium have been mentioned in this section. Additional information on a large number of compounds has been summarized by Cunningham.[26]

34. Coprecipitation behavior of plutonium. Concentrations of plutonium too small to exceed the solubility product of any plutonium compound can nevertheless be removed from aqueous solution by coprecipitation with certain carrier compounds. In general, these carrier compounds are related to the plutonium compounds of low solubility. Table 17 gives an indication of the coprecipitation behavior of the three most important oxidation states of plutonium. The data on this topic are very extensive and can only be touched upon briefly in this article. Certain of the more important purification or analytical procedures based upon coprecipitation will be discussed briefly.

The differing behavior of the oxidation states makes possible a very high degree of separation from unwanted impurities by successive precipitation of the carrier compound under different oxidation conditions. Many impurities which coprecipitate with the plutonium can be removed by a "by-product" precipitation of the carrier compounds after adjustment of the oxidation state of the plutonium to a state which does not coprecipitate.

The lanthanum fluoride cycle was used in the very earliest studies of plutonium and is still extensively used in laboratory scale studies.

Table 17. Coprecipitation Behavior of Trace Amounts of Plutonium

Carrier Compound	Pu(III)	Pu(IV)	Pu(VI)
Insoluble hydroxides	C	C	C
Lanthanum fluoride	C	C	NC
Phosphates:			
Zirconium phosphate	NC	C	NC
Bismuth phosphate	C	C	NC
Thorium pyrophosphate	NC	C	NC
Thorium hypophosphate		C	NC
Oxalates:			
Thorium oxalate	C	C	NC
Uranium(IV) oxalate	C	C	NC
Bismuth oxalate	C	C	NC
Lanthanum oxalate	C	C	NC
Iodates:			
Zirconium iodate		C	NC
Thorium iodate		C	NC
Ceric iodate		C	NC
Sodium uranyl acetate	NC	NC	C
Zirconium phenylarsonate	NC	C	NC
Thorium peroxide		C	
Bismuth arsonate		C	NC

The letter C indicates that coprecipitation is nearly quantitative under suitable conditions. The letters NC mean that coprecipitation may easily be made less than 1 to 2 percent under proper conditions.

Neutron-irradiated uranium is dissolved in nitric acid, and lanthanum fluoride is precipitated after reduction of the plutonium with sulfur dioxide. The precipitate "carries" plutonium and some of the fission products, particularly the rare earths. The mechanism of carrying of plutonium(IV) on LaF_3 is the formation of anomalous mixed crystals.[30a] The lanthanum is put back into solution and reprecipitated after oxidation of the plutonium to the non-coprecipitated hexapositive state. The rare-earth impurities are removed with this "by-product" lanthanum fluoride precipitate. Neptunium and plutonium can be separated by taking advantage of differences in the rates of oxidation of the two elements to the hexavalent state, neptunium being more quickly oxidized than plutonium. Bromate ion at room temperature has frequently been used for this selective oxidation of neptunium.

[30a] K. Schlyter and L. G. Sillén, Acta Chem. Scan. 4, 1323 (1950).

In the zirconium phosphate cycle the oxidation state of plutonium is adjusted to plutonium(IV), for example, by treatment with hot concentrated nitric acid, and zirconium phosphate is precipitated to carry the plutonium. The plutonium is put back into solution and oxidized to the hexapositive form. Zirconium phosphate is again precipitated to remove phosphate insoluble impurities while plutonium remains in solution.

Neptunium and plutonium can be separated with zirconium phosphate by treatment of the solution with a hydrazine - ferrous ion mixture before precipitation. Plutonium is reduced to the non-carryable (III) state while neptunium is reduced only to the (IV) state which carries quantitatively.

Zirconium phenylarsonate is very useful in radiochemical analyses because of its specificity for the removal of tetravalent cations from solution. It is superior to zirconium phosphate in this respect. It can be used to measure the percentage of plutonium present in solution as plutonium(IV) in a mixture of ion species, or it can be used to carry out the separation of neptunium(IV) from plutonium(III), or zirconium(IV) from plutonium(VI) or for similar separations.

These coprecipitation separations are discussed more completely elsewhere.[31]

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[31] E. K. Hyde, Chapter 15, N.N.E.S. Vol. 14A, "The Actinide Elements," 1954; E. K. Hyde, Paper P/728, "Proceedings of the Geneva Conference--Peaceful Uses of Atomic Energy," August 1955, United Nations.

35. The bismuth phosphate process. One of the early industrial processes suggested for the isolation of plutonium is based on bismuth phosphate and lanthanum fluoride as carrier precipitation agents. This process was originally conceived by S. G. Thompson, G. T. Seaborg, and their collaborators at the Metallurgical Laboratory of the University of Chicago during World War II.[32] Neutron-irradiated uranium is dissolved in nitric acid and treated with sodium nitrite to fix the plutonium oxidation state at plutonium(IV). Sulfuric acid and nitric acid concentrations are adjusted to prevent precipitation of uranyl phosphate after which bismuth phosphate is precipitated. Plutonium(IV) is coprecipitated quantitatively in spite of the fact that the amount of bismuth left in solution is rather high. Plutonium(III) is carried much less completely than plutonium(IV) in spite of the greater structural similarity of plutonium(III) phosphate to bismuth phosphate. The bismuth phosphate is dissolved in concentrated nitric acid. (The ease of separation of bismuth phosphate precipitates and their relative ease of dissolution were important factors in the choice of bismuth phosphate.) Sodium bismuthate is used to oxidize plutonium(IV) to plutonium(VI). A by-product bismuth phosphate precipitate is then formed to remove phosphate insoluble fission-product impurities leaving oxidized plutonium in solution. Plutonium in the solution is reduced again to plutonium(IV) and coprecipitated with bismuth phosphate. This decontamination cycle is repeated. At this point the carrier is changed to lanthanum fluoride. A lanthanum-fluoride oxidation reduction cycle is gone through for further decontamination but principally for concentration. The final product-bearing lanthanum fluoride precipitate is metathesized to lanthanum hydroxide and dissolved in acid. The plutonium at this point is sufficiently concentrated that final purification can be done without the use of carrier compounds.

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[32] S. G. Thompson and G. T. Seaborg, "The First Use of Bismuth Phpsphate for Separating Plutonium from Uranium and Fission Products," Progress in Nuclear Energy, Series 3, Volume 3, "Process Chemistry," edited by F. R. Bruce, J. M. Fletcher, H. H. Hyman, and J. J. Katz, Pergamon Press Ltd., 1956.

36. Solvent extraction of plutonium. Plutonium resembles the other actinide elements in that a number of organic solvents immiscible with water are capable of extracting it from acidic aqueous solutions. Such extractions are very useful in the separation of plutonium from most of the elements in the periodic system. The differing extraction behavior of the different oxidation states can be a powerful aid in these separations. A list of some of the more carefully investigated solvents given in Table 18 indicates the general type of solvents which are most effective.

Table 18. Organic Solvents Capable of Extracting Plutonium from Aqueous Solution.

ethyl ether
tributyl phosphate (TBP)
diisopropyl ketone
methyl isobutyl ketone ("hexone")
methyl n-amyl ketone

diethyl cellosolve
dibutyl carbitol
dibutoxytetraethylene glycol ("pentaether")
triglycol dichloride

Ethyl ether is chiefly used for the extraction of plutonium(VI) from nitric acid solutions containing a high concentration of nitrate salts such as ammonium nitrate, calcium nitrate, magnesium nitrate or aluminum nitrate. The extraction is highly specific for hexapositive actinide element ions, except for a very few elements such as the halogens, and is widely used in laboratory research with trace amounts of plutonium.

The other solvents listed in Table 18 exhibit much higher distribution coefficients for plutonium in the tetrapositive and hexapositive oxidation states. For this and a variety of other reasons they are more suitable for large scale or industrial scale use. Tributyl phosphate (TBP) extraction will be discussed to show the effect of a number of variables important in determining the extent of plutonium extraction. TBP is usually diluted to a 15 - 40 percent solution in inert solvents as kerosene, butyl ether, or carbon tetrachloride to improve the physical characteristics of the solvent. Data quoted here will be for 20 percent solutions.

The extraction of the actinide element ions from nitrate aqueous systems into TBP increases in the order:

Plutonium ions	Pu(III) $\ll$ Pu(VI) $<$ Pu(IV)	
Tetrapositive ions	Th(IV) $<$ Np(IV) $<$ Pu(IV)	High extractability
Hexapositive ions	Pu(VI) $<$ Np(VI) $<$ U(VI)	High extractability
Pentapositive ions	Np(V) Limited data indicates very low extractability	
Tripositive ions	Pu(III) $<$ Am(III) $<$ Cm(III) $<$ etc.	Low extractability

Some sample data are given in Table 19.

Table 19. Distribution Ratio, $E_{aq.}^{org.}$, for Plutonium Extraction into Tributyl Phosphate (20 percent solution in kerosene).

Aqueous Composition	Pu(III)[1]	Pu(IV)[2]	Pu(VI)[1]
1 M HNO_3	0.01	1.5	0.7
3 M HNO_3	-	6.8	2.26
6 M HNO_3	0.01	19.6	2.86
10 M HNO_3	-	13	2.27
1 M HNO_3, 3 M $NaNO_3$	-	19.0	-
1 M HNO_3, 5 M $NaNO_3$	-	62	-

[1] J. M. Fletcher, Paper P/413, "Proceedings of the Geneva Conference--Peaceful Uses of Atomic Energy," August 1955, United Nations.

[2] H. A. C. McKay, ibid., Paper P/441.

Increasing the nitric acid concentration increases the distribution coefficient, but it is much more effective to increase the concentration of sodium nitrate or other neutral nitrate salts because of the high extractability of the complex $HNO_3 \cdot TBP$ which competes with the plutonium-solvent complex. Furthermore, extraction of impurity ions is much greater in highly acidic systems. Hence extraction may be carried out with concentrated salt systems with just enough nitric acid present to be certain that no hydrolysis of plutonium occurs or else from rather dilute nitric acid solutions without other salting agents. Complexing agents for plutonium such as fluoride, oxalate, sulfate, or phosphate ion will interfere with the extraction.

The fission product elements most difficult to separate by solvent extraction are cerium, zirconium, niobium, iodine, and ruthenium.

Plutonium may be separated conveniently from neighboring elements by solvent extraction. Uranium can be extracted away from plutonium by reduction of the latter to unextractable plutonium(III); alternatively an organic solvent solution of the two can be contacted with a nitrate salt solution containing a reducing agent capable of reducing plutonium to plutonium(III). A neptunium-plutonium aqueous mixture is easily separated by treatment with a reducing agent to produce a mixture of neptunium(IV) and plutonium(III). The neptunium is then extracted leaving the plutonium behind. Separation of plutonium from americium(III) or higher elements is simple after plutonium is oxidized to a higher oxidation state.

In industrial practice solvent extraction is performed in packed columns or pulsed columns or in a series of mixing-settling chambers in which the aqueous phase and solvent phase pass in counter current flow in a multi-stage process. Such systems incorporate a back-washing scrub section in which impurities with lower distribution coefficients than the desired product are returned to the aqueous phase.

In the industrial process known as the "Redox" process uranium and plutonium are separated from fission products and from each other by extraction with methyl n-butyl ketone (hexone). The uranium nitrate dissolver solution is oxidized and contacted with hexone to extract uranium(VI) and plutonium(VI). The hexone layer is scrubbed with an acid deficient aluminum nitrate solution to remove impurities. The hexone is then contacted with an aluminum nitrate solution containing a reducing agent which does not affect the uranium but reduces the plutonium to plutonium(III) and strips it into the aqueous phase. The plutonium product from this cycle is oxidized to prepare it for reextraction and the entire sequence of extraction as oxidized plutonium followed by reduction and stripping as tripositive plutonium is repeated once or twice more.

In the industrial "Purex" process, TBP diluted with a kerosene type solvent is used. The uranium slugs are dissolved in nitric acid, plutonium is fixed as plutonium(IV) and the acid strength is adjusted so that plutonium(IV) and uranium(VI) are coextracted away from the fission products. Impurities are backwashed with a nitric acid solution flowing countercurrent to the solvent stream. In a second part of the process, the solvent is contacted with a nitric acid solution containing a reducing agent. Uranium(VI) is left in the TBP phase while plutonium(III) is removed. Both uranium and plutonium are put through additional purification before complete purification is achieved.

A detailed discussion of such processes is beyond the scope of this article; more information can be found elsewhere.[33,34]

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[33] F. L. Culler, Paper P/822, "Proceedings of the Geneva Conference--Peaceful Uses of Atomic Energy," August 1955, United Nations.

[34] Progress in Nuclear Energy, Series 3, Volume 3, "Process Chemistry," edited by F. R. Bruce, J. M. Fletcher, H. H. Hyman, and J. J. Katz, Pergamon Press Ltd., 1956.

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37. Solvent extraction of chelate complexes of plutonium. A very sizeable number of organic compounds are known which form compounds with aqueous ions of plutonium which are insoluble or which can be extracted from aqueous solution into non-polar organic solvents. Many of these such as the alpha-hydroxquinolinate, the nitrobenzoate, or the pyrogallate are useful in analysis. A widely used reagent cupferron (the ammonium salt of nitrosophenylhydroxylamine) forms a compound with plutonium(IV) which is extractable into chloroform. Rydberg[34a] has made extensive studies on the acetylacetone complexes of plutonium and other heavy elements.

[34a] J. Rydberg, Arkiv för Kem. 9, No. 8, 109 (1955).

The beta diketone, alpha-thenoyltrifluoroacetone, usually referred to as TTA, forms a chelate compound with plutonium(IV) which is very stable and highly extractable into non-polar solvents even from strongly acidic solutions. The equilibrium quotients for complex formation between TTA and various metal ions cover the enormous range from 10^{10} to 10^{-15}. Since plutonium(IV) is among the most strongly complexed ions, the extraction of the TTA-plutonium complex separates plutonium to a very high degree from most impurities including the tripositive actinide or lanthanide elements. From acidic solution the principal contaminating ions are zirconium(IV), hafnium(IV), iron(III), cerium(IV), tin(IV), and niobium(V). Among the heavy elements protactinium(V), thorium(IV), uranium(IV), and neptunium(IV) are extracted. The acid dependence of the extraction is very high (fourth power for tetrapositive ions) and by adjustment of acidity and TTA concentration very sensitive control of the extraction is possible. Hence even those elements with similar equilibrium quotients can be separated. Complexing agents inhibit the extraction of the plutonium(IV).

Plutonium(IV) is readily separated from uranium(VI) as the extraction of the latter under acidic conditions into non-polar solvents is slight. Plutonium is separated from neptunium by TTA extraction under reducing conditions when neptunium(IV) is extracted into the solvent layer leaving plutonium(III) in the aqueous phase.

An industrial process has been studied for the recovery of plutonium and uranium from reactor fuel elements based on the use of TTA extraction.[33]

38. Ion exchange behavior of plutonium. It was mentioned in Section 25 under neptunium chemistry that negatively charged complexes of plutonium(VI) and plutonium(IV) are formed in concentrated solutions of hydrochloric acid and that these complexes are readily adsorbed by anion exchange resins. Plutonium(VI) also forms negatively charged nitrate complexes in concentrated solutions of nitric acid which are adsorbed on anion exchange resins. The importance of these properties was discussed in Section 25.

Plutonium in all its oxidation states is readily adsorbed on cation exchange resins from dilute acid solution. Highest adsorbability is achieved for the tetrapositive state. This property is of considerable use in concentration of plutonium from large volumes of solution and in the removal of non-cationic impurities. Plutonium may be separated from other cations by selective elution from columns packed with cation exchange resin. Oxalic acid, citric acid, lactic acid, sulfate ion, ethylenediamine tetraacetic acid, and other complexing agents have been used. Since negatively charged chloride complexes of plutonium are formed in moderately concentrated hydrochloric acid such solutions readily elute plutonium from cation exchange resins.

This is shown dramatically in Figure 15. In this figure data of Diamond, Street, and Seaborg[35] are used. In a series of experiments trace amounts of thorium, uranium, neptunium, and plutonium in various oxidation states were adsorbed on Dowex-50 cation exchange resin and eluted with hydrochloric acid; the elution of the radioactive ions was followed by radiochemical analysis. The relative position of the elution peaks constructed from this series of experiments are presented on Figure 15 on a logarithmic scale. The separations shown may not be quantitatively reproducible but the schematic representation of the relative elution order is believed to be correct.

Figure 15. Summary of elution peak position of thorium, uranium, neptunium, and plutonium in various oxidation states showing the effect of hydrochloric acid concentration on the elution of the elements.
Data taken from Diamond, Street, and Seaborg.[35]

The behavior of the tetrapositive ions is particularly striking. Thorium(IV) is a comparatively large, highly charged, unoxygenated ion and adheres very strongly to the resin. In fact, the mass action effect of hydrogen ion in any concentration of hydrochloric acid is not sufficient to elute it at a convenient rate. Uranium(IV), neptunium(IV), and plutonium(IV), however, show an increasing tendency toward chloride complex formation and plutonium(IV) in particular can be desorbed rather quickly with concentrated hydrochloric acid.

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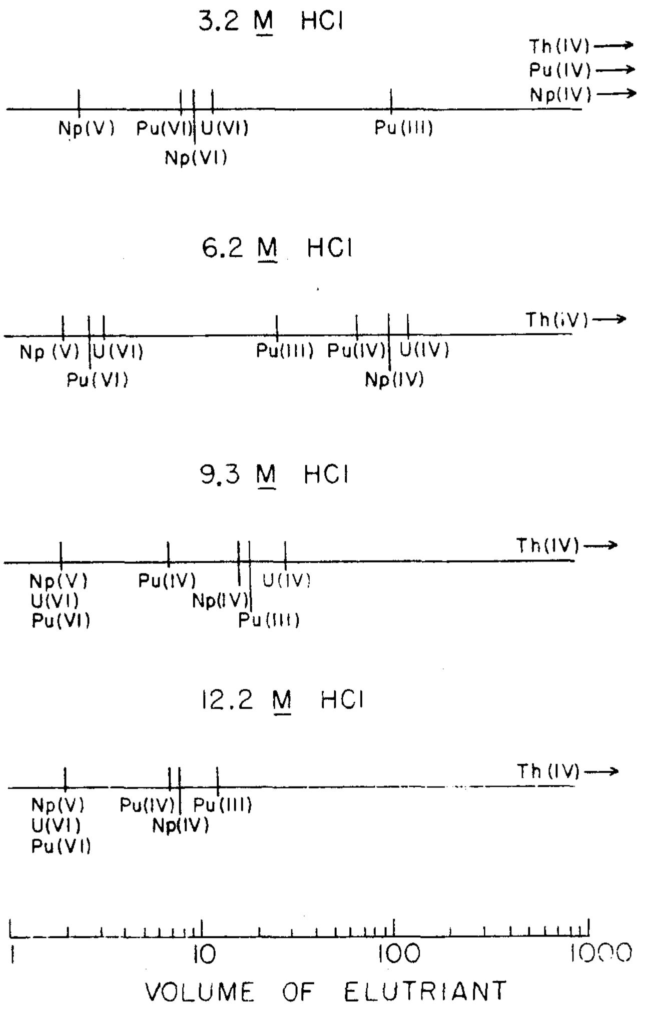
[35] R. M. Diamond, K. Street, Jr., and G. T. Seaborg, J. Am. Chem. Soc. 76, 1461 (1954).



MU-9900

Figure 15

III. AMERICIUM (ELEMENT 95)

a. History of Americium

39. Discovery of americium--summary of known isotopes. Americium was the fourth transuranium element to be discovered, its first identification at the wartime Metallurgical Laboratory of the University of Chicago by Seaborg, James, Morgan, and Ghiorso[36,37] taking place late in 1944 and early in 1945. The first isotope to be discovered was Am^{241}, formed by intense neutron irradiation of plutonium in nuclear reactors according to the reactions $Pu^{239}(n,\gamma)Pu^{240}(n,\gamma)Pu^{241}$ followed by $Pu^{241} \xrightarrow[13\ \text{years}]{\beta^-} Am^{241}$. The isotope Am^{241} decays by the emission of alpha particles with a half life of 470 years. The element was named americium, symbol Am, in honor of the Americas. This name was chosen to point up the strong analogy between element 95 and its homologue, europium, named after Europe, of the lanthanide rare earth series. Americium does not occur in nature.

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[36] G. T. Seaborg, R. A. James, and L. O. Morgan, Paper 22.1, N.N.E.S. Vol. 14B, "The Transuranium Elements," 1949.

[37] A. Ghiorso, R. A. James, L. O. Morgan, and G. T. Seaborg, Phys. Rev. 78, 472 (1950).

Americium was first isolated in the form of a pure compound by B. B. Cunningham[38] at the Metallurgical Laboratory in 1945. Plutonium which is isolated from reactor fuel elements that have been subjected to intensive neutron irradiation contains an appreciable amount of Pu^{241}. Hence plutonium is a convenient source of americium because upon standing Am^{241} grows into the plutonium. Gram quantities of Am^{241} can now be prepared in this way.

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[38] B. B. Cunningham, Paper 19.2, N.N.E.S., Vol. 14B, "The Transuranium Elements," 1949.

A large number of americium isotopes have been prepared by the bombardment of heavy element targets in cyclotrons or by intense neutron irradiation of plutonium or americium samples in reactors. These isotopes and their principal decay characteristics are listed in Table 20. Decay schemes of the more carefully studied isotopes are given in Figure 16.

Figure 16. Decay schemes of americium isotopes.

The isotope Am^{243} is worth special mention because it is more stable (half life 8800 years) than Am^{241}. This is important because the study of the chemistry of americium using Am^{241} is severely hindered by the remarkable chemical effects caused by the intense alpha radiation of Am^{241}; the specific activity is 7×10^{13} disintegrations per minute per gram. Most chemical studies up until 1954 were of necessity performed with Am^{241}. Increasing use of Am^{243} is certain as milligram and largerquantities become more generally available. The isotope Am^{243} can be prepared nearly pure isotopically by a sequence of neutron bombardments and chemical separations as follows: The bombardment of Am^{241} with neutrons yields Pu^{242} by the reactions $Am^{241}(n,\gamma)Am^{242m} \xrightarrow{\text{electron capture}} Pu^{242}$; after chemical separation the Pu^{242} can be transformed to Am^{243} via the reactions $Pu^{242}(n,\gamma)Pu^{243} \xrightarrow[\text{hours}]{\beta^-} Am^{243}$, and the Am^{243} can be chemically separated. An alternate sequence is to prepare Pu^{242} of fairly high isotopic purity by intense neutron irradiation of Pu^{239}, purify it and return it to the reactor for conversion to Am^{243} via the sequence:

$$Pu^{242}(n,\gamma)Pu^{243};Pu^{243} \xrightarrow[\text{5.0 hours}]{\beta^-} Am^{243}.$$

b. Chemical Properties of Americium

We have noted the decreasing stability of the higher oxidation states in the sequence uranium-neptunium-plutonium. In americium we reach the first element for which the tripositive state characteristic of an actinide series is the most stable solution state. For some time after its discovery the tripositive state was the only solution state for which there was reliable evidence. Later, extensive evidence for other oxidation states was found as described below. For curium and all the higher actinide elements the tripositive state is the only solution state except for berkelium which can be oxidized to berkelium(IV).

Table 20 Isotopes of Americium*

Isotope and Half-Life	Type of Decay	Energy (Mev)	Method of Production	Disintegration Energies (Mev)†
Am^{238}	EC		Pu^{239} d-3n	Q_{EC}=2.25(est.)
1.86 h	γ	.98, .58, .102(Ref. 1)	Pu^{239} p-2n	Q_{α} =6.02(est.)
Am^{239}	EC 99^{+}%		Np^{237} α-2n	Q_{EC}=0.86(calc.)
12 h	α $4.1x10^{-3}$%	5.78	Pu^{239} p-n	Q_{α} =5.93
	γ(with α)	.048	Pu^{239} d-2n	
	γ(with EC)	.04940, ,05725, .06782, .1818, .2099, .2264, .2284, .2777, .2856 deduced from Np^{239} decay scheme (Ref. 13)	Pu^{239} α-p3n	
Am^{240}	EC		Np^{237} α-n	Q_{EC}=1.44(est.)
50h	γ	.92(14%), 1.02(70%), 1.40(15%).(Ref. 3)	Pu^{239} d-n Pu^{239} α-p2n	Q_{α} =5.78(est.)
Am^{241}	α	5.535(0.34%), 5.503(0.21%) 5.476(84.2%), 5.433(13.6%) 5.379(1.4%),[5.321(0.015%) 5.241?(0.002%) (Ref. 12)]	Pu^{239} multiple n capture	Q_{α}=5.63
470 y α	β stable		daughter Pu^{241}	I =5/2
	γ	.02636, .03320⁺, .04346, .056, .05957⁺, .099, .103, .113, .130, .159, .165, .210, .270, .328, .370, .430, (Ref. 4) (See also Ref. 15, 16, 17) +metastable $t_{1/2}$ =6.3x 10^{-8}sec Coulombic excitation of Np^{237} produces levels at 0.332 and .076 Kev (Ref. 14).		
Am^{242m}	β^- 81%	.620	Pu^{239} multiple n capture	Q_{β^-} =0.62
16.01 h	EC 19%		Am^{241} n-γ	Q_{EC}=0.67
	IT ≤6%			Q_{α} =5.53(calc.)
	γ	.0422, ,0446 (Ref. 11)		

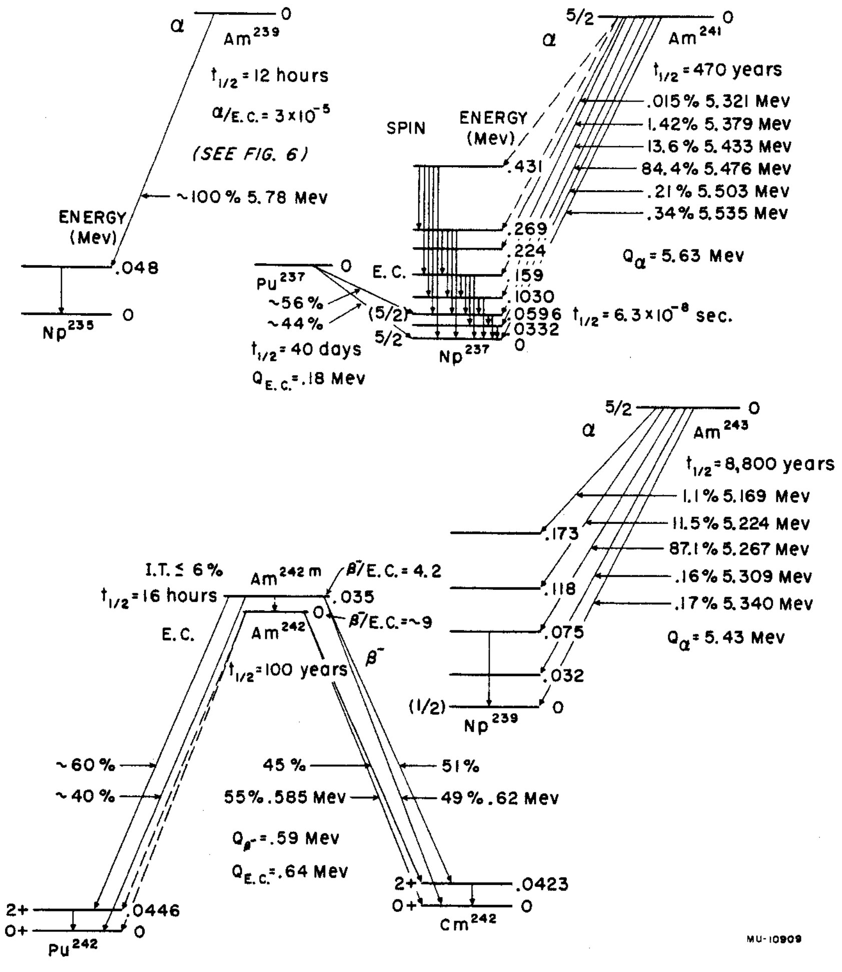
α
0
Am²³⁹
t1/2 = 12 hours
α/E.C. = 3×10⁻⁵
(SEE FIG. 6)
~100 % 5.78 Mev
ENERGY (Mev)
.048
0
Np²³⁵
5/2
0
α
Am²⁴¹
t1/2 = 470 years
.015 % 5.321 Mev
1.42 % 5.379 Mev
13.6 % 5.433 Mev
84.4 % 5.476 Mev
.21 % 5.503 Mev
.34 % 5.535 Mev
Qα = 5.63 Mev
SPIN
ENERGY (Mev)
.431
.269
.224
.159
.1030
.0596
.0332
0
t1/2 = 6.3×10⁻⁸ sec.
E. C.
Pu²³⁷
0
~56 %
~44 %
(5/2)
5/2
Np²³⁷
t1/2 = 40 days
QE.C. = .18 Mev
5/2
0
α
Am²⁴³
t1/2 = 8,800 years
1.1 % 5.169 Mev
11.5 % 5.224 Mev
87.1 % 5.267 Mev
.16 % 5.309 Mev
.17 % 5.340 Mev
Qα = 5.43 Mev
.173
.118
.075
.032
(1/2)
0
Np²³⁹
I.T. ≤ 6 %
t1/2 = 16 hours
Am²⁴² m
β⁻/E.C. = 4.2
.035
Am²⁴²
0
β⁻/E.C. = ~9
E.C.
t1/2 = 100 years
β⁻
~60 %
~40 %
45 %
55 % .585 Mev
51 %
49 % .62 Mev
Qβ⁻ = .59 Mev
QE.C. = .64 Mev
2+
0+
.0446
0
Pu²⁴²
2+
0+
.0423
0
Cm²⁴²
MU-10909

Figure 16

Isotope and Half-Life	Type of Decay	Energy (Mev)	Method of Production	Disintegration Energies (Mev)
Am^{242} 100 y	β^- 90% EC 10%	.585 (Ref. 5) .0422, .0446 (Ref. 5)	Am^{241} n-γ	$Q_{\beta^-}=0.59$ $Q_{EC}=0.64$ $Q_\alpha=5.50$(calc.)
Am^{243} 8800 y 7600 y (Ref. 10)	α β stable γ	5.340(0.17%), 5.309(0.16%), 5.267(87.1%), 5.224(11.5%) 5.169(1.1%) (Ref. 6) .075	Am^{242} n-γ Pu^{239} multiple n capture	$Q_\alpha=5.43$ I =5/2
Am^{244} 26 m	β^- >94% EC 3.9×10^{-2}% (Ref.18)	1.5 (Ref. 7)	Am^{243} n-γ	$Q_\alpha=5.34$(calc.) $Q_{\beta^-}=1.50$
Am^{245} 1.98 h	β^- (Ref. 8) γ	.905 (Ref. 8) .036, .120, .143, .156, .232, .255 (Ref. 8)	Pu^{239} multiple n capture Pu^{244} n-γ (Ref. 8)	$Q_{\beta^-}=0.90$ $Q_\alpha=5.17$(est.)
Am^{246} 25m	β^- (Ref. 9) γ	1.2 (Ref. 9) .019, .103, .795, 1.069 (Ref. 9)	Pu^{239} multiple n capture (Ref. 9)	$Q_{\beta^-}=2.29$ $Q_\alpha=5.00$(est.)

*For references to original data not given specifically here, refer to Hollander, Perlman, and Seaborg, "Table of Isotopes", Rev. of Mod. Physics 25, 469 (1953) and to the compilations of the Nuclear Data Group, National Research Council.

†Revised values from Glass, Thompson, and Seaborg., J. Inorg.and Nucl. Chem. 1, 3 (1955).

1. R. J. Carr, reported in University of California Radiation Laboratory Report UCRL-2455 (Jan. 1954).
2. W. M. Gibson, unpublished data, private communication (Jan. 1956).
3. R. A. Glass, Ph.D. Thesis, University of California Radiation Laboratory Report UCRL-2560 (April 1954).
4. P. P. Day, Phys. Rev. 97, 689 (1955); see also H. Jaffe, et. al., Phys. Rev. 97, 142 (1955).
5. T. O. Passell, Ph.D. Thesis, University of California Radiation Laboratory Report UCRL-2528 (March 1954).
6. F. S. Stephens, et. al., Phys. Rev. 98, 261A (1955).
7. A. Ghiorso, et. al., Phys. Rev. 94, 1081 (1954).
8. C. I. Browne, et. al., J. Inorg. and Nuc. Chem. I, 254 (1955).
9. D. Engelkemeir, et. al., J. Inorg. and Nuc. Chem. I, 345 (1955).

10. I. Perlman, et. al., University of California Radiation Laboratory Report UCRL-3068 (July 1955).
11. R. W. Hoff, et. al., Phys. Rev. 100, 1403 (1955).
12. L. L. Goldin, E. F. Tretyakov, G. I. Novikova, pp. 226-249, Proceedings of the Moscow Conference on Atomic Energy, July 1-5, 1955.
13. J. M. Hollander, et. al., University of California Radiation Laboratory Report UCRL-3222 (Sept. 1955).
14. J. O. Newton, Nature 175, 1028 (1955).
15. J. M. Hollander, W. G. Smith and J. O. Rasmussen, University of California Radiation Laboratory Report UCRL-3239 (1955); Phys. Rev. (1956).
16. Milsted, Rosenblum and Valadares, Compt. rend. 239, 259, 700 (1954).
17. S. A. Baranov and K. N. Shlyagin, Proceedings of Moscow Meeting on Atomic Energy (July 1955) p. 252.
18. P. R. Fields, et al, Phys. Rev. 100, 172 (1955).

40. Americium metal. Americium is a highly electropositive element and the reduction of compounds to the metal can be effected only under anhydrous conditions with powerful reducing agents such as the alkali and alkaline earth metals. For example, Westrum and Eyring[39] reduced AmF_3 with barium vapor at 1200° C. The measured density of americium metal is 11.7 ± 0.3 g/cm^3.[39] The structure of americium from x-ray studies[39a] is double hexagonal close-packed with a = 3.642 ± 0.005 Å and c = 11.76 ± 0.01 Å. The americium radius is 1.82 Å and the calculated density is 11.87 ± 0.05 g/cm^3 in excellent agreement with the experimental value. Americium is the first of the transuranium elements to resemble the lanthanide elements closely in the metallic state. Data on americium metal are summarized in Table 21.

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[39] E. F. Westrum, Jr. and L. Eyring, J. Am. Chem. Soc. 73, 3396 (1951).

[39a] P. Graf *et al.*, University of California Radiation Laboratory Report UCRL-3280 (1956), submitted for publication in J. Am. Chem. Soc. (1956).

Table 21. Thermodynamic Properties of Americium Metal

Melting point	Softens at 850° C; incomplete melting at 1200° C (ref. 1)
Heat of reaction with 1.5 M HCl	-162.3 ± 2.7 Kcal mole^{-1} (ref. 2)
Heat of formation at 25°C of Am^{+3}(aq.)	-163.2 ± 2.7 Kcal mole^{-1}(ref. 1, 2)
Formal potential for the reaction $Am \longrightarrow Am^{+3}(aq) + 3e^-$	+2.32 ± 0.04 est. (ref. 2)
Vapor pressure	$\log p = 7.563 - 13{,}162/T$ over range 1103 to 1453° K (ref. 3). Assuming ΔC_p of vaporization = -2 cal $\text{mole}^{-1}\text{deg}^{-1}$ $\log p = 11.092 - 13{,}700/T - \log T$.
Free energy of vaporization	$\Delta F = 62{,}690 - 50.76T - 2.303(-2)T\log T$ (ref. 3).
Heat of vaporization at 1273° K	$\Delta H_{1273} = 60.2$ Kcal mole^{-1} (ref. 3)

[1] E. F. Westrum, Jr. and L. Eyring, J. Am. Chem. Soc. 73, 3396 (1951).

[2] B. B. Cunningham and H. R. Lohr, J. Am. Chem. Soc. 73, 2026 (1951).

[3] S. C. Carniglia and B. B. Cunningham, J. Am. Chem. Soc. 77, 1502 (1955).

41. Americium(II). Because of the special stability of the half-filled electron configuration $5f^7$ it might be expected that americium(II) by analogy to samarium(II) would be stabilized enough to permit its observation. Fragmentary evidence[40] for the apparent production of americium(II) has not been confirmed and strenuous efforts to produce it under conditions which readily converted samarium and ytterbium to the dipositive state have all failed.[41] A limit of $>$ +1.5 volts has been set on the Am^{+2} - Am^{+3} couple.

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[40] S. G. Thompson, L. O. Morgan, R. A. James, and I. Perlman, Paper 19.1, N.N.E.S. Vol. 14B, "The Transuranium Elements," 1949.

[41] R. A. Penneman and L. B. Asprey, Paper P/838, "Proceedings of the Geneva Conference--Peaceful Uses of Atomic Energy," August 1955, United Nations.

Americium metal reacts with a deficiency of oxygen to yield AmO,[42] a compound which is metallic and not ionic in character and similar to NpO and PuO. Similarly a metallic hydride of the formula AmH_2 is known.[42]

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[42] F. H. Ellinger, unpublished work cited by R. A. Penneman and L. B. Asprey, Reference 41.

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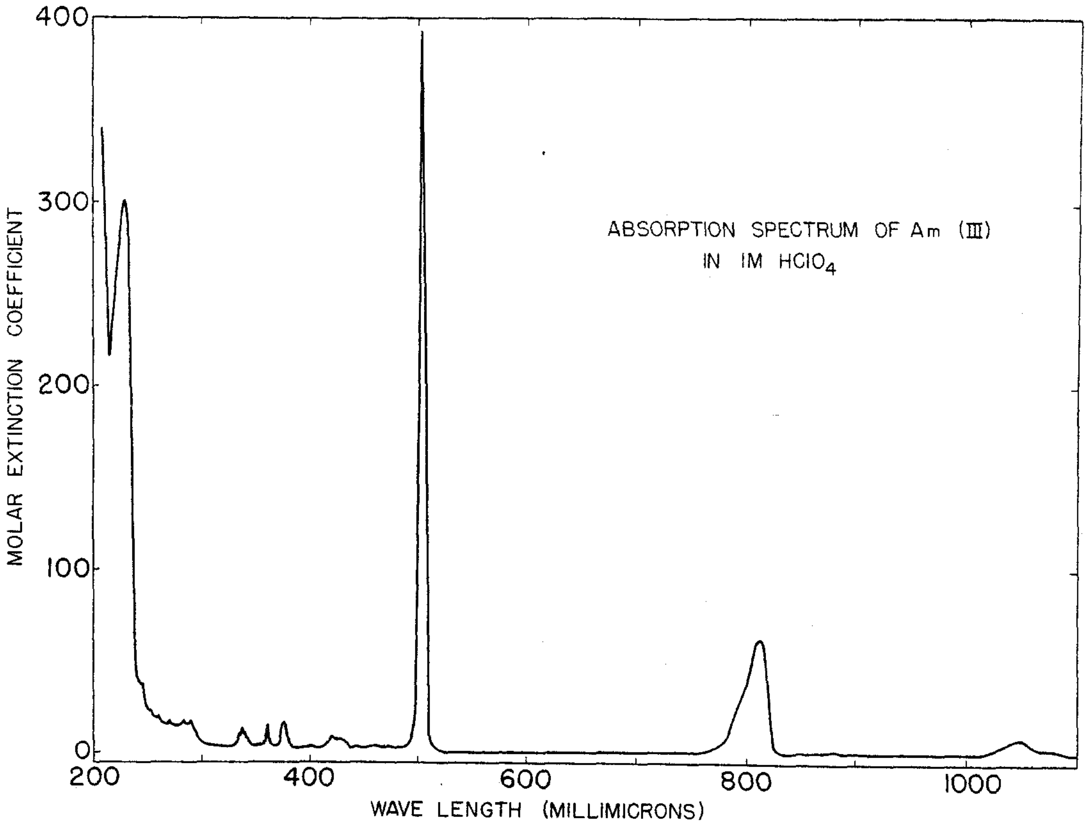
42. Americium(III). Americium(III) forms a pink-colored solution in dilute acids changing to yellow as the concentration is increased. The absorption spectrum of americium(III) is shown in Figure 17. The absorption peak at 503 millimicrons is so sharp that instrumental defects can cause deviations from the Beer-Lambert law when it is used for analysis. The peaks at 503 and 812 millimicrons are somewhat similar to europium(III) but have much greater extinction coefficients which indicates greater influence of the environment on the 5f electrons. The sharp absorption

Figure 17. Absorption spectrum of americium(III) in 1 M perchloric acid.
S. E. Stephanou, J. P. Nigon, and R. A. Penneman, J. Chem. Phys. 21, 42 (1953).



MU-10961

Figure 17

line at 503 millimicrons was shown to resolve into four very sharp lines when it was measured with a grating spectrograph.[43] In strong nitric acid or sulfuric acid marked changes in the extinction coefficients and slight shifts of the major peaks occur because of complexing.[44]

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[43] B. J. Stover, J. G. Conway, and B. B. Cunningham, J. Am. Chem. Soc. 73, 491 (1951).

[44] G. N. Yakovlev and V. N. Kosyakov, Paper P/676, "Proceedings of the Geneva Conference--Peaceful Uses of Atomic Energy," August 1955, United Nations.

The principal compounds of low solubility are the hydroxide, the fluoride, oxalate, and phosphate. The resemblance in structure and solubility of the americium compounds and the rare earth compounds is quite close. The crystal radius of Am^{+3} is nearly the same as that of neodymium. Such compounds as lanthanum trifluoride are commonly used to carry trace concentrations of americium. The separation of tripositive americium from tripositive rare earths can be done by fractional precipitation of certain compounds, for example, the oxalates.[45]

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[45] J. A. Hermann, Los Alamos Scientific Laboratory Report LADC-1687 (1954).

The most powerful method for the separation of tripositive americium from the rare earths is the ion exchange elution method. A mixture of americium and rare earth activities can be adsorbed from dilute acid solution on a column of cation resin such as Dowex-50 and then by selective elution with buffered citrate, lactate, hydroxyisobutyrate, ethylenediamine tetraacetic acid or similar agents the elements can be separated. The rare earth element promethium is the most difficult to separate as its elution behavior under most conditions is quite similar to that of americium.

A more satisfactory separation is achieved if 13 molar hydrochloric acid is used as the eluting agent. Americium and curium and the other tripositive actinide elements elute well ahead of the first rare-earth element (lutetium) to come off the column. This elution is rather interesting when the elution position of americium with respect to curium is considered.

It is found that as the molarity of hydrochloric acid is changed the relative order of elution changes. In 13 molar acid americium elutes first indicating a stronger tendency to form chloride complexes. This behavior of americium and curium has been interpreted as arising from covalent bonding involving 5f orbitals which become accessible for some of the actinide elements.[46]

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[46] R. M. Diamond, K. Street, Jr., and G. T. Seaborg, J. Am. Chem. Soc. 76, 1461 (1954).

Tripositive americium and curium are poorly extracted by the organic solvents which we have previously discussed for the higher oxidation states of neptunium and plutonium (Table 18, Section 36). However, under certain conditions appreciable distribution coefficients between acidic aqueous solutions and undiluted tri-n-butyl phosphate can be achieved. In Figure 18 the extraction coefficients of tripositive actinide and rare-earth elements are given for extraction into tributylphosphate from 12 M hydrochloric acid and 15 M nitric acid. These extraction coefficients are sufficiently different that neighboring elements such as americium and curium can be separated from each other by proper adjustment of conditions.[47]

Figure 18. Distribution coefficients for the extraction of tripositive lanthanide and actinide elements into tributyl phosphate from (A) 12 N hydrochloric acid and (B) 15.6 N nitric acid.

Unpublished data, D. F. Peppard, Argonne National Laboratory and P. R. Gray, University of California.

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[47] D. F. Peppard, P. R. Gray, and M. M. Markus, J. Am. Chem. Soc. 75, 6063 (1953).

Other methods of purifying americium which depend upon oxidation to a higher oxidation state will be discussed later.

43. Americium(IV). This oxidation state is well known in the solid state as will be discussed in Section 46, but there is no evidence for americium(IV) in aqueous solution. This fact is understandable since the oxidation potential of the americium(III) - americium(IV) couple in acid solution is estimated to be -2.44 volts.[48]

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[48] L. Eyring, H. R. Lohr, and B. B. Cunningham, J. Am. Chem. Soc. 74, 1186 (1952).

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44. Americium(V). This oxidation state was first prepared by oxidizing americium(III) in potassium carbonate solution using sodium hypochlorite.[49] Americium(V) precipitates as a double carbonate salt of americium and potassium. Alternate oxidizing agents are ozone or peroxydisulfate ion.[50,51] The compound can be dissolved in dilute acid to give a solution of americium(V) with a characteristic absorption spectrum. Slow reduction to americium(III) occurs from the reducing effects of the alpha radiation; in strong acid extensive disproportionation occurs. Tracer amounts of americium can be oxidized in carbonate solution and removed quantitatively from solution by precipitating potassium uranyl carbonate or potassium plutonyl carbonate as a carrier compound.[51] Excellent separation from rare earths and many impurities is achieved.

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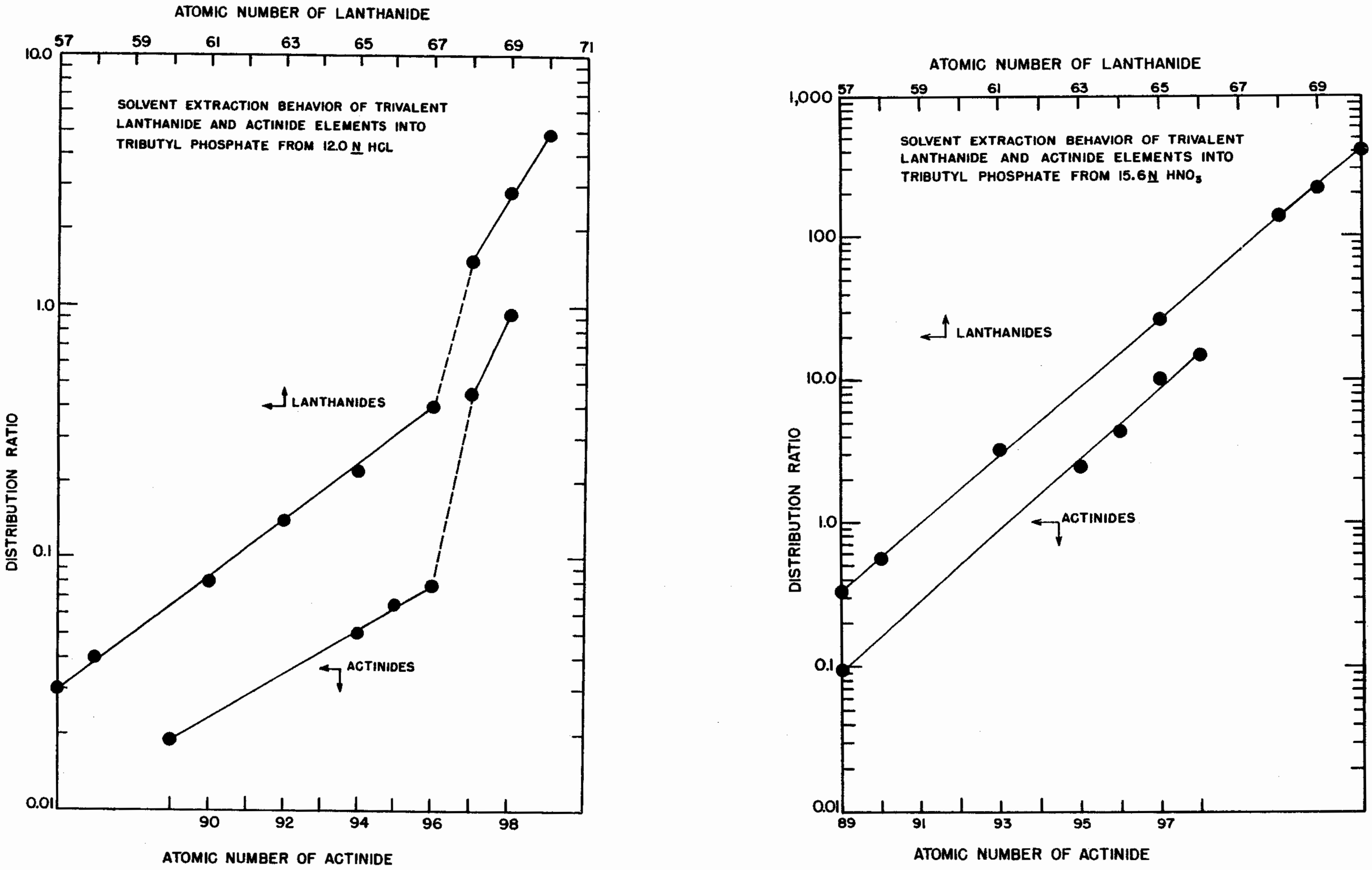
[49] L. B. Werner and I. Perlman, J. Am. Chem. Soc. 73, 495 (1951).

[50] S. E. Stephanou, J. P. Nigon, and R. A. Penneman, J. Chem. Phys. 21, 42 (1953).

[51] G. N. Yakovlev and D. S. Gorbenko.Germanov, Paper P/677, "Proceedings of the Geneva Conference--Peaceful Uses of Atomic Energy," August 1955, United Nations.

Americium(V) may also be prepared by reduction of americium(VI) with chloride ion or bromide ion. Solutions of americium(VI) simply on standing are reduced at a rate of approximately 4 percent per hour because of the reducing effects of the alpha radiation. No reduction to americium(III) occurs until the hexapositive ion has disappeared completely. Gunn[52] prepared pure solutions of americium(V) by passing americium(VI) in 1 M $HClO_4$ through a short column of Dowex-50 cation exchange resin. The resin



MU-4742

MU-4741

Figure 18

instantly reduced the americium to americium(V) which passed through the column while any americium(III) impurity was strongly adsorbed on the resin.

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[52] S. Gunn, thesis, University of California Radiation Laboratory, declassified report UCRL-2541.

Several lines of evidence strongly suggest that AmO_2^+ is the ionic species in acidic solution. The similarity in chemistry of americium(V) and PuO_2^+ and NpO_2^+ is large. The solid compounds $RbAmO_2CO_3$ and $NH_4AmO_2CO_3$ have been isolated[53] and identified by x-ray analysis.[54] Infrared spectrum studies favor the AmO_2^+ structure for the ion. The reversibility of the (V) - (VI) couple is evidence for a simple electron transfer mechanism and hexavalent americium is believed to be AmO_2^{++}.

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[53] J. P. Nigon *et al.*, J. Phys. Chem. 58, 403 (1954).

[54] F. H. Ellinger and W. H. Zachariasen, J. Phys. Chem. 58, 405 (1951).

The absorption spectrum of americium(V) has been determined in perchloric acid, hydrochloric acid, and sulfuric acid media by many laboratories. Figure 19 shows the spectrum in 1 molar perchloric acid where complexing is slight. The peak at 717 millimicrons is used in analysis.

Figure 19. Absorption spectrum of americium(V) in 1 M $HClO_4$.
S. E. Stephanou, J. P. Nigon, and R. A. Penneman, J. Chem. Phys. 21, 42 (1953).

Photospectrometry has been used to follow the disproportionation of americium(V) in perchloric acid,[52,55] in hydrochloric acid,[56] and in sulfuric acid.[57] Strong acid is required for appreciable disproportionation; this is in sharp constrast to the disproportionation of plutonium(V). The rate curves for disproportionation in 6 M perchloric acid are given in Figure 20. The disappearance of americium(V) is second order with respect

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Figure 20. The disproportionation of americium(V) in 6 M $HClO_4$.
From S. E. Stephanou, J. P. Nigon, and R. A. Penneman, J. Chem. Phys. 21, 42 (1953).

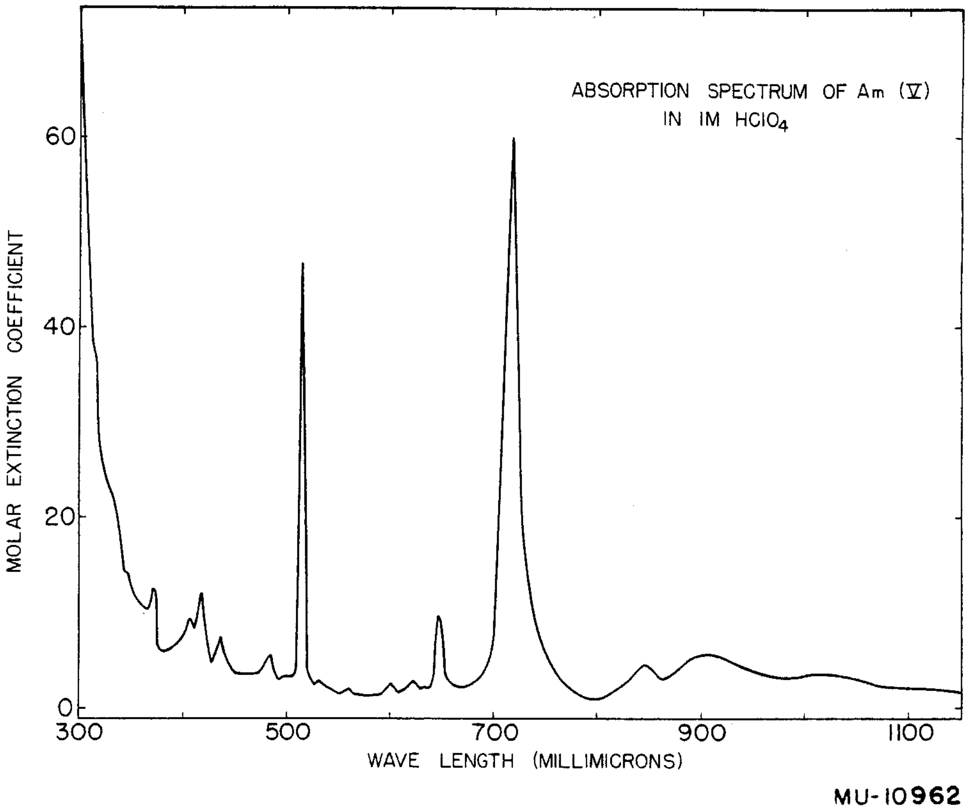
ABSORPTION SPECTRUM OF Am (V)
IN 1M HClO4
MOLAR EXTINCTION COEFFICIENT
0
20
40
60
300
500
700
900
1100
WAVE LENGTH (MILLIMICRONS)
MU-10962

Figure 19

to the concentration of americium(V) and fourth order with respect to the hydrogen ion concentration so the rate determining step is written:

$$2\mathrm{AmO}_2^+ + 4\mathrm{H}^+ \rightleftharpoons \mathrm{AmO}_2^{+2} + [\mathrm{Am(IV)}] + 2\mathrm{H}_2\mathrm{O} \qquad (41.1)$$

The americium(IV) is postulated although no spectral evidence for it is seen. It is immediately destroyed by reduction by water, by radiation-produced reducing agents, or by the reaction:

$$\mathrm{Am}^{+4} + \mathrm{AmO}_2^+ \longrightarrow \mathrm{Am}^{+3} + \mathrm{AmO}_2^{+2}. \qquad (41.2)$$

Combining this last equation the overall equation for disproportionation is

$$3\mathrm{AmO}_2^+ + 4\mathrm{H}^+ \rightleftharpoons 2\mathrm{AmO}_2^{+2} + \mathrm{Am}^{+3} + 2\mathrm{H}_2\mathrm{O}. \qquad (41.3)$$

True disproportionation equilibrium is never reached because of self-reduction effects of the alpha particles and eventually all of the americium is converted to americium(III).

The self-reduction of Am^{241}(V) solutions is roughly two percent per hour in perchloric acid[52,55] or sulfuric acid.[57] The rate of self-reduction is appreciably lower in 0.5 molar hydrochloric acid.[56] Marked reduction of this rate is achieved when reagents are added to destroy hydrogen peroxide, one of the breakdown products from water chiefly responsible for the reduction.[52]

In pure solutions of the longer-lived isotope, 8800-year Am^{243}, the self-reduction effects interfere to a lesser degree with a study of the chemistry of americium.

45. Americium(VI). This oxidation state was first established by Asprey, Stephanou, and Penneman.[58] Americium(III) in dilute acid solution can be converted to pale-yellow americium(VI) by peroxydisulfate ion or by argentic ion. Oxidation by ceric ion is incomplete; oxidation by

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[55] S. E. Stephanou, L. B. Asprey, and R. A. Penneman, Atomic Energy Commission Unclassified Document AECU-925 (1950).

[56] G. R. Hall and P. D. Herniman, J. Chem. Soc. 2214 (1954).

[57] G. N. Yakovlev and V. N. Kosyakov, Paper P/676, "Proceedings of the Geneva Conference--Peaceful Uses of Atomic Energy," August 1955, United Nations.

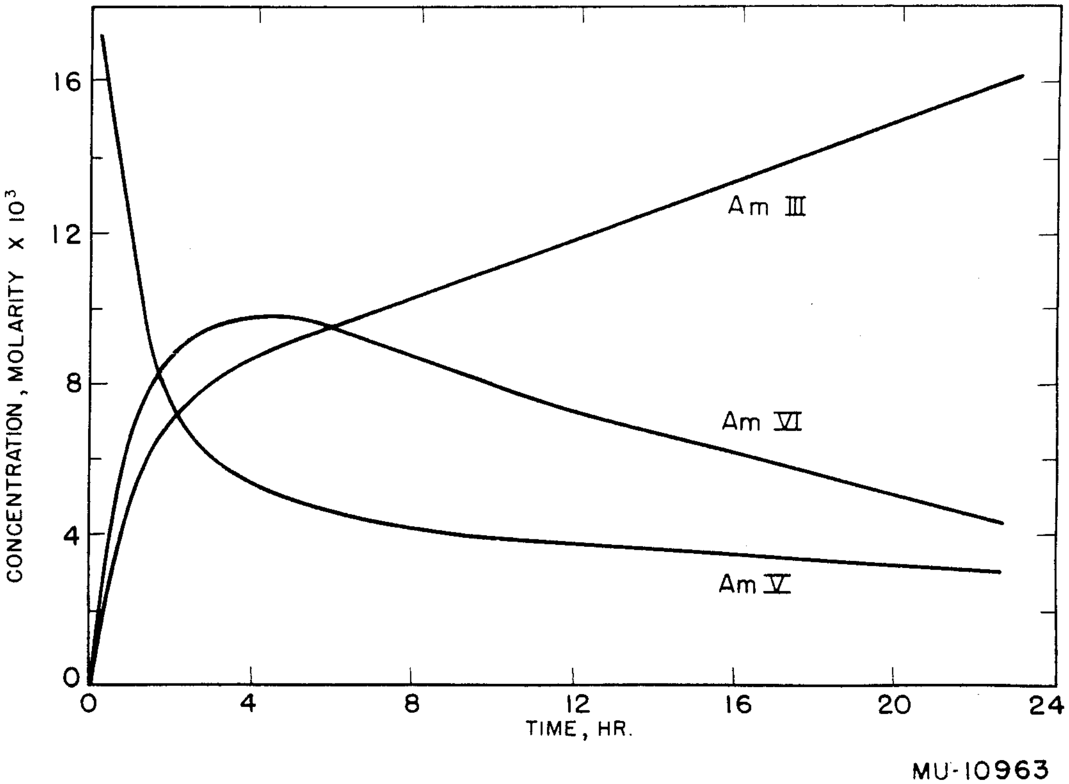
CONCENTRATION, MOLARITY X 10^3
16
12
8
4
0
0
4
8
12
16
20
24
TIME, HR.
Am III
Am VI
Am V
MU-10963

Figure 20

ozone and periodic acid is unsuccessful, but anodic oxidation is successful.

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[58] L. B. Asprey, S. E. Stephanou, and R. A. Penneman, J. Am. Chem. Soc. 72 1425 (1950) and J. Am. Chem. Soc. 73, 5715 (1951).

Asprey and Penneman[59] report that quantitative oxidation of americium(III) to americium(VI) with peroxydisulfate ion has been carried out in solutions varying between 10^{-8} M and ~ 0.2 M in americium. The reaction is no more than first order with respect to americium. It is quite essential that the hydrogen ion concentration be kept low to prevent the acid-catalyzed breakdown of peroxydisulfate ion with the ultimate formation of hydrogen peroxide, a reducing agent for americium(VI). A suggested set of conditions are: $H^+ \leq 0.1$ molar; $S_2O_8^=$ = 0.2 to 0.5 molar; temperature 90° C; time ~ 15 minutes. This oxidation can be carried out in perchloric, nitric or sulfuric acid but not in hydrochloric acid.

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[59] R. A. Penneman and L. B. Asprey, report P/838 "Proceedings of the Geneva Conference--Peaceful Uses of Atomic Energy," August 1955, United Nations.

Americium(V) may be converted to americium(VI) by ozone oxidation in hot perchloric or nitric acid. Cerium(IV) and argentic ion are also effective in this oxidation. Disproportionation of americium(V) in strong acid converts part of it to americium(VI).

Electrolytic oxidation to americium(VI) is incomplete and erratic in a simple cell but Gunn obtained rapid and near quantitative oxidation in a three-compartment cell with the americium placed only in the anode compartment.[52] One molar nitric acid, 1 molar perchloric acid or 6 molar perchloric acid could be used at 0° C.

The chemical behavior of americium(VI) is very similar to that of uranium(VI), neptunium(VI), and plutonium(VI) and the ionic species is undoubtedly AmO_2^{+2}. Insoluble fluorides may be precipitated in its presence (preferably with KF) to remove fluoride insoluble impurities. Organic solvents such as ethyl ether and methyl isobutyl ketone will extract americium(VI) from aqueous solution.

The absorption spectrum of AmO_2^{+2} in perchloric acid is given in Fig. 21.

Figure 21. The absorption spectrum of americium(VI) in 1 M $HClO_4$.
S. E. Stephanou, J. P. Nigon, and R. A. Penneman, J. Chem. Phys. 21, 42 (1953).

The peaks at ~ 995 and 1667 millimicrons are used in analysis.

The formal potential for the AmO_2^+ - AmO_2^{+2} couple was found to be -1.60 volts by measurements against the cerium(III) - cerium(IV) couple in 1 M perchloric acid and against Hg_2^{+2} - Hg^{+2} in 1 M perchloric acid using shiny platinum electrodes.[60] A study[61] of the oxidation of americium(III) to americium(VI) by cerium(IV) yielded the value of -1.67 for the half reaction:

$$Am^{+3} + 2H_2O \rightleftharpoons AmO_2^{+2} + 4H^+ + 3e^- \qquad (42.1)$$

An indirect measurement of Gunn[52] based upon the measurement of the heat of reduction of americium(VI) with ferrous ion and the use of previously known and estimated thermodynamic quantities gave -1.70 volts as the potential for this reaction.

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[60] R. A. Penneman and L. B. Asprey, U.S. Atomic Energy Commission Unclassified Report AECU-936 (1950).

[61] J. P. Nigon, unpublished work, Los Alamos Scientific Laboratory, reported by Penneman and Asprey, Paper P/838, Reference 59.

Figure 22 is an oxidation potential scheme for americium in acid solution. In this scheme the (III) - (VI) couple is shown as -1.69 volts rather than as either of the two values just cited for internal consistency reasons. The values for the Am - Am^{+2} couple and for the Am^{+4} - AmO_2^+ couple were obtained simply by difference.

Figure 22. Formal potential scheme for americium in acid solution.

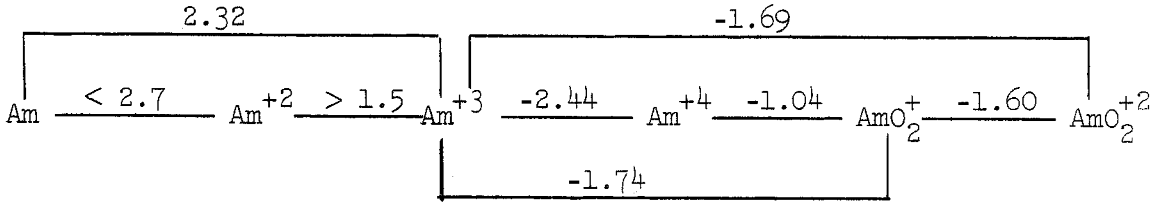

Figure 23 is an oxidation potential scheme given by Latimer[62] for basic solution. These are estimated rather than experimental values.

Figure 23. Potential scheme for americium in basic solution.

$$Am \xrightarrow{2.71} Am(OH)_3 \xrightarrow{0.4} Am(OH)_4 \xrightarrow{(-0.7)} AmO_2OH \xrightarrow{(-1.1)} AmO_2(OH)_2$$

46. <u>The anhydrous compounds of americium</u>. When americium is precipitated as the insoluble hydroxide from aqueous solution and heated in air a black oxide is formed with the formula AmO_2. This may be reduced to orange-red Am_2O_3 through the action of hydrogen at elevated temperatures. The AmO_2 has the fluorite type structure, isostructural with UO_2, NpO_2, and PuO_2. The Am_2O_3 has the cubic sesquioxide structure typical of the rare-earth elements. A second crystal modification of Am_2O_3 is cubic.[63] See Table 6, Section 6.

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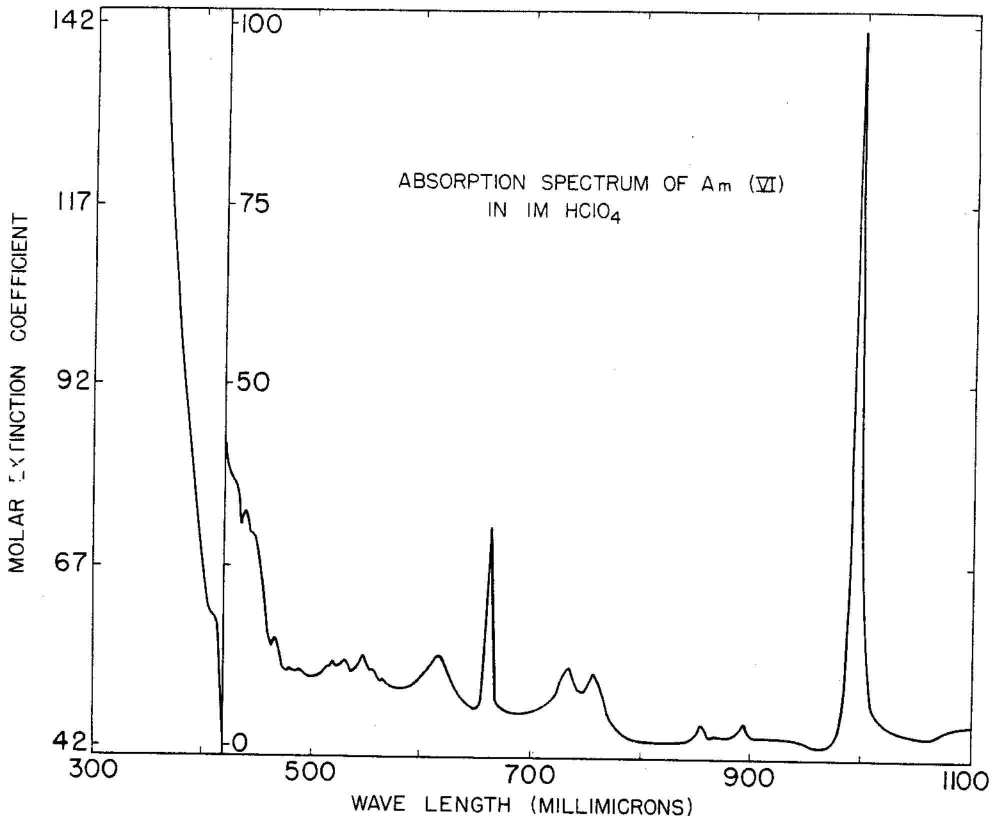
[62] Wendell M. Latimer, "Oxidation Potentials," Second Edition, Prentice Hall Inc., New York (1952), p. 311.

[63] D. H. Templeton and C. H. Dauben, J. Am. Chem. Soc. 75, 4561 (1953).



MU-10964

Figure 21

The halogen compounds of americium were first prepared by Fried.[64] Pink americium trichloride has been prepared by treating AmO_2 at 800 - 900° C with carbon tetrachloride and with gaseous hydrogen chloride. Its vapor phase hydrolysis to the oxychloride AmOCl has been studied carefully.[65] The oxychloride is isostructural[63] with PuOCl and PrOCl. Americium tribromide, $AmBr_3$, has been prepared by carrying out the following reaction in a sealed tube at 500° C.

$$3AmO_2 + 4AlBr_3 \longrightarrow 3AmBr_3 + 2Al_2O_3 + 3/2\ Br_2 \tag{46.1}$$

Americium triiodide was made by a similar reaction. When americium dioxide is treated with oxygen-hydrogen fluoride mixtures at 600 - 750° C pink americium trifluoride is produced whereas neptunium or plutonium dioxides under similar circumstances are converted to the tetrafluoride. Asprey[66] succeeded in preparing americium tetrafluoride by reacting americium dioxide or trifluoride with fluorine gas at one atmosphere pressure and 500° C. Asprey also prepared $KAmF_5$ by fluorine treatment of $KAmO_2CO_3$. All of these halogen compounds have been characterized crystallographically and are isostructural with the analogous plutonium compounds

The only hexapositive compound of definitely known composition and structure is the lemon-yellow sodium americyl acetate, $NaAmO_2(C_2H_3O_2)_3$, isostructural with similar compounds of uranium, neptunium, and plutonium.

Among pentapositive americium compounds $RbAmO_2CO_3$, $NH_4AmO_2CO_3$, and $KAmO_2F_2$ have been identified by x-ray analysis.[53,54,66a].

Lattice constants for a number of crystalline americium compounds are given in Table 6, Section 6.

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[64] S. Fried, J. Am. Chem. Soc. 73, 416 (1951).

[65] C. Koch and B. B. Cunningham, J. Am. Chem. Soc. 76, 1470 (1954).

[66] L. B. Asprey, J. Am. Chem. Soc. 76, 2019 (1954).

[66a] L. B. Asprey, F. H. Ellinger, and W. H. Zachariasen, J. Am. Chem. Soc. 76, 5235 (1953).

IV. CURIUM (ELEMENT 96)

47. Discovery of curium--summary of known isotopes. The first isotope of element 96 to be found was Cm^{242} which was identified in 1944 by Seaborg, James, and Ghiorso[67] among the products of the bombardment of a Pu^{239} target with 32-Mev helium ions. The Cm^{242} was made by the reaction $Pu^{239}(\alpha,n)Cm^{242}$ reaction. The discovery of curium preceded that of americium. The first isolation of curium in the form of a pure compound was made by Werner and Perlman in 1947.[68]

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[67] G. T. Seaborg, R. A. James, and A. Ghiorso, Paper 22.2, N.N.E.S. Vol. 14B, "The Transuranium Elements," 1949.

[68] L. B. Werner and I. Perlman, Paper 22.5, N.N.E.S. Vol 14B, "The Transuranium Elements," 1949.

The name curium was chosen to emphasize the analogy between the rare-earth element gadolinium which contains seven 4f electrons and element 96 which contains the same number of 5f electrons. Gadolinium was named indirectly after J. Gadolin, the great Finnish investigator of the rare-earth elements; curium was named after Pierre and Marie Curie, famous investigators in the field of natural radioactivity. Curium is of some special interest because it completes the first half of the actinide transition series.

The isotope, Cm^{242}, can also be prepared in a nuclear reactor by the reaction sequence:

$$Am^{241}(n,\gamma)Am^{242m};\ Am^{242m} \xrightarrow[16\text{ hours}]{\beta^-} Cm^{242}. \qquad (44.1)$$

One can also start with plutonium, thus:

$$Pu^{239}(n,\gamma)Pu^{240}(n,\gamma)Pu^{241} \xrightarrow[13\text{ years}]{\beta^-} Am^{241}(n,\gamma)Am^{242m} \xrightarrow[16\text{ hours}]{\beta^-} Cm^{242}. \quad (44.2)$$

Larger amounts can be prepared in these ways for chemical studies than can be made in cyclotrons.

The isotope, Cm^{242}, decays by the emission of alpha particles (the energy of the most prominent group being 6.110 Mev) with a half life of 162.5 days. This is about the half life of polonium which is 138.3 days. In both elements chemical studies are highly hindered by physiological hazards and by chemical effects of the intense alpha radiation. The specific activity of Cm^{242} is about 10^{14} alpha disintegrations per minute per milligram. Water solutions of Cm^{242} are decomposed by this radiation; some of the decomposition products such as hydrogen peroxide interfere with attempted chemical reactions. Precise temperature control of solutions or compounds, as for example, in magnetic susceptibility experiments is difficult because of heating effects. A massive chunk of such curium metal would be heated instantly to incandescence even if it could be prepared; the energy released is 1230 watts per gram. Crystal lattices of compounds are disarranged by recoil effects of the alpha particles.

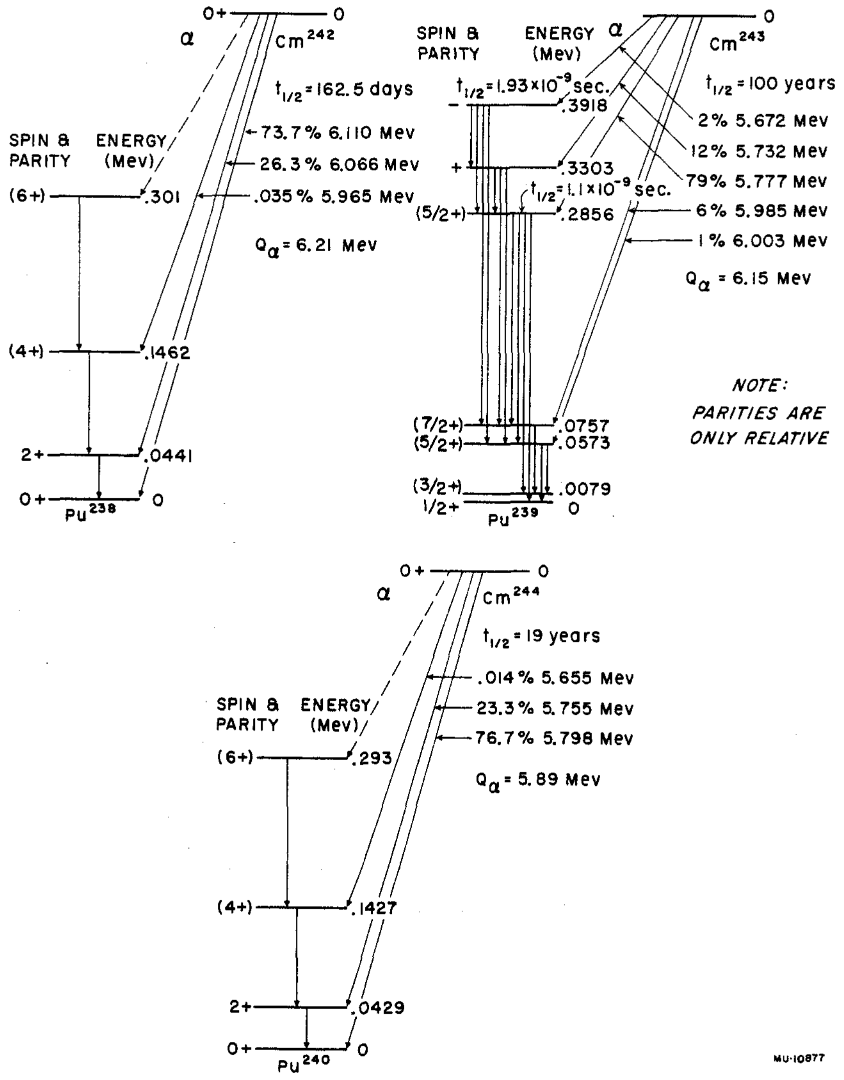
At the present time all the curium isotopes of mass number 238 to 249 are known. Those lighter than 243 may be prepared by bombardment of plutonium with very high energy helium ions. Those higher in mass number are made by neutron capture or multiple neutron capture reactions in high flux reactors starting with plutonium or curium isotopes of lower mass. The principal decay characteristics of these isotopes are given in Table 22. Decay schemes for those curium isotopes which have been most carefully studied are given in Figure 24.

Figure 24. Decay schemes of curium isotopes.

The isotope Cm^{244} has a particular importance for chemical studies because it can be prepared with rather high isotopic purity in milligram or greater quantities. The half life is 19.4 years and the specific alpha activity is 43 times less than that of Cm^{242}. It can be made in a high flux reactor via the neutron capture sequence:

$$Pu^{239}(n,\gamma)Pu^{240}(n,\gamma)Pu^{241}(n,\gamma)Pu^{242}(n,\gamma)Pu^{243} \xrightarrow[5.0\ hr]{\beta^-} Am^{243}(n,\gamma)Am^{244} \xrightarrow[26\ min]{\beta^-} Cm^{244}. \tag{44.3}$$

Chemical purification of the Am^{243} (which may also be prepared as described in section 39) may be desirable before the final transmutation to curium. A sample of 350 milligrams of Pu^{239} irradiated to a total neutron flux of 10^{22} neutrons in the Materials Testing Reactor in Idaho resulted in the production of a minimum of 3 milligrams of curium with the isotopic composition 1.84 percent Cm^{242}, 95.5 percent Cm^{244}, 1.27 percent Cm^{245},



0+
0
α
Cm^{242}
$t_{1/2}$ = 162.5 days
73.7% 6.110 Mev
26.3% 6.066 Mev
.035% 5.965 Mev
Q_α = 6.21 Mev
SPIN & PARITY
ENERGY (Mev)
(6+) .301
(4+) .1462
2+ .0441
0+ 0
Pu^{238}
SPIN & PARITY
ENERGY (Mev)
α
0
Cm^{243}
$t_{1/2}$ = 100 years
$t_{1/2}$ = 1.93×10^{-9} sec.
− .3918
+ .3303
$t_{1/2}$ = 1.1×10^{-9} sec.
(5/2+) .2856
2% 5.672 Mev
12% 5.732 Mev
79% 5.777 Mev
6% 5.985 Mev
1% 6.003 Mev
Q_α = 6.15 Mev
NOTE: PARITIES ARE ONLY RELATIVE
(7/2+) .0757
(5/2+) .0573
(3/2+) .0079
1/2+ 0
Pu^{239}
0+
0
α
Cm^{244}
$t_{1/2}$ = 19 years
.014% 5.655 Mev
23.3% 5.755 Mev
76.7% 5.798 Mev
Q_α = 5.89 Mev
SPIN & PARITY
ENERGY (Mev)
(6+) .293
(4+) .1427
2+ .0429
0+ 0
Pu^{240}
MU-10877

Figure 24

Table 22 Isotopes of Curium*

Isotope and Half-Life	Type of Decay	Energy (Mev)	Method of Production	Disintegration Energies (Mev) †
Cm^{238} 2.5 h	EC<90% α >10%	 6.50	Pu^{239} α-5 n	Q_{EC}=1.09(est.) Q_{α}=6.63
Cm^{239} ~3 h	EC~100%		Pu^{239} α-4 n	Q_{EC}=1.74(est.) Q_{α}=6.50(est.)
Cm^{240} 26.8 da 1.9×10^6 y spon. fiss.	α	6.25	Th^{232} C-4 n Pu^{239} α-3 n	Q_{EC}=0.08(est.) Q_{α}=6.38
Cm^{241} 35 d	EC 99^{+}% α 0.96% (Ref. 1) γ	 .472 (Ref. 1)	Pu^{239} α-2 n	Q_{EC}=0.85(est.) Q_{α}=6.30(est.)
Cm^{242} 162.5 da 7.2×10^6 y spon. fiss.	α β stable γ	6.110(73.7%), 6.066(26.3%) 5.965(0.035%) .044, .100, .157 (Ref. 2) .210, .562, .605 (Ref. 5) .0441 0.1019 .1577 (Ref. 11)	Pu^{239} α-n Am^{241} d-n daughter Am^{242} daughter Cf^{246}	Q_{α} =6.21
Cm^{243} 35y	α β stable γ	6.003(1%), 5.985(6%), 5.777(79%), 5.732(12%) 5.672(2%)(Ref. 9) .04464, .04940, .05725, .0614 .06782, .1061, .2099, .2284, .2546, .2731, .2777, .2856, .3161, .3345 deduced from Np^{239} decay scheme (Ref. 10)	Cm^{242} n-γ daughter Bk^{243}	Q_{α} =6.19

Isotope and Half-Life	Type of Decay	Energy (Mev)	Method of Production	Disintegration Energies (Mev)[†]
Cm^{244} 19 y α 1.4 x 10^7 y spon. fiss.	α β stable γ	5.798(76.7%), 5.755(23.3%) 5.655(.014%) .043, .100, .150, (Ref. 5) .0429 (Ref. 11)	Cm^{243} n-γ daughter Am^{244}	Q_α =5.89
Cm^{245} 2x10^4 y (Ref. 3) 1.4x10^4 y (Ref. 8) 1.2x10^4 y (Ref. 4)	α β stable γ	5.36 (Ref. 3) .101(80%), .173(13%)(Ref. 5)	Pu^{239} multiple n capture daughter Bk^{245} Cm^{244} n-γ	Q_α =5.62
Cm^{246} 4000 y (Ref. 4) 2300 y (Ref. 8) 3x10^7 y spon. fiss.	α β stable	5.36(Ref. 4)	Cm^{245} n-γ	Q_α =5.45
Cm^{247} (Ref. 6) >60 d	β stable		Pu^{239} multiple n capture	Q_α =5.25(est.)
Cm^{248} (Ref. 7) long lived	β stable		Pu^{239} multiple n capture	Q_α =5.17(est.)
Cm^{249} (Ref. 7) short	β^- (Ref. 7)		Pu^{239} multiple n capture	Q_β=1.09(est.) Q_α=5.29(est.)

[*] For references to original data not given specifically here, refer to Hollander, Perlman and Seaborg "Table of Isotopes", Rev. of Mod. Physics, 25, 469 (1953) and to the compilations of the Nuclear Data Group, National Research Council.

[†] Revised values from Glass, Thompson, and Seaborg, J. Inorg. and Nucl. Chem. 1, 3 (1955).

1. R. A. Glass and J. W. Cobble, unpublished data (1954).
2. F. Asaro, et al. Phys. Rev 92, 694 (1953).
3. E. K. Hulet, et al., Phys. Rev. 95, 1703 (1954).
4. A. M. Friedman, et al., Phys. Rev. 95, 1501 (1954).
5. I. Perlman, et al., University of California Radiation Laboratory Report No. UCRL-2932, (March 1955) and UCRL-3068, (July 1955).

6. C. M. Stevens, et al., Phys. Rev. 94, 974 (1954).
7. W. C. Bentley, et al., Paper P/809 "Peaceful Uses of Atomic Energy-Proceedings of the Geneva Conference" United National (August 1955).
8. C. I. Browne, et al., J. Inorg, and Nuc. Chem. I, 254 (1955).
9. F. Asaro, private communication (1956).
10. J. M. Hollander, et al., University of California Radiation Laboratory Report No. UCRL-3222(Sept. 1955). Phys. Rev. May 1, 1956
11. W. G. Smith and J. M. Hollander, University of California Radiation Laboratory Report No. UCRL-2974 Rev. 1955; To Phys. Rev. January 15, 1956.

1.36 percent Cm^{246}, and 0.016 percent Cm^{247}.[68a] Further neutron irradiation of Cm^{244} produces larger percentages of the higher mass isotopes, Cm^{245} and Cm^{246} of longer half life which are even better for use in chemical investigations.

[68a] C. M. Stevens et al., Phys. Rev. 94, 297 (1954).

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48. Chemical properties of curium in aqueous solution. Most investigations of curium have been carried out with the tracer technique. In aqueous solution curium is present in the tripositive state, and no reliable evidence for any other solution state has ever been found. A variety of the strongest oxidizing agents such as dichromate, permanganate, peroxydisulfate, argentic ion, and others gave no indication of oxidation under a variety of conditions. Failure to observe oxidation conceivably could be due to slow reaction at tracer concentration so many experiments were repeated at concentration of about 10^{-5} molar with similar results. In solutions containing mixtures of Am^{241} and Cm^{242} it has been possible to oxidize americium to americium(V) in a carbonate solution or to oxidize it to americium(VI) in an acid solution without oxidizing any of the curium. Experiments with Cm^{244} solutions similarly show no evidence for oxidation. It seems unlikely that curium will ever be found in aqueous solution as curium(IV), curium(V), or curium(VI). Any reasonable extrapolation of the increase of the (III)-(IV) or the (III)-(V), or the (III)-(VI) couples with atomic number shows that this must be so. (See for example, Figure 2, Section 2.)

Tripositive curium closely resembles the other tripositive actinide and lanthanide ions. It is readily coprecipitated with rare-earth fluorides, oxalates, and hydroxides. In macroscopic concentrations curium trifluoride precipitates directly upon addition of hydrofluoric acid. The chloride, bromide, iodide, perchlorate, nitrate, and sulfate are soluble. Separation from rare earths is moderately difficult and is best carried out by the cation exchange method. The mixture of activities is adsorbed from dilute acid solution on top of a column of Dowex-50 resin (a copolymer of styrene and divinyl benzene containing nuclear sulfonic acid groups) or other suitable resin. Elution with 13 molar hydrochloric acid quickly removes curium (and americium and other tripositive actinide elements if present) well ahead of the rare earths. (See Figure 30, Section 55) Alternative, but not as effective, eluting agents for the curium - rare earth separation are buffered solutions of citric acid, lactic acid, or alpha-hydroxyisobutyric acid. Column operations with Cm^{242} are complicated by bubble formation in the solutions due to the alpha activity when amounts greater than 10 micrograms are used. A partial solution is to increase the diameter of the column and to increase the flow rate.

Removal of americium impurity is a problem of frequent occurrence in curium chemistry which may be solved in a variety of ways. For a long time the best method was selective elution from cation-resin columns with buffered citric, lactic, tartaric, or alpha-hydroxyisobutyric acid. See figure 25 which shows that complete separation is possible. Americium and curium extract into tributyl phosphate from concentrated hydrochloric acid or nitric acid with appreciable distribution coefficients.[69] See Figure 18, Section 42. These coefficients are sufficiently different for the two elements that a good separation is possible. When larger amounts of americium are handled it is convenient to take advantage of the upper oxidation states of americium. Oxidation with peroxydisulfate ion in dilute acid at 70 - 95° C for a few minutes followed by rapid precipitation of a small amount of lanthanum fluoride to carry the curium has been reported by S. E. Stephanou and R. A. Penneman.[70] Gunn[71] suggests anodic oxidation at 0° C to americium(VI) at a platinum anode with the active solution in an isolated anode compartment in dilute nitric acid or perchloric acid solution; after oxidation a quick precipitation of lanthanum fluoride removes curium. Yakovlev and Gorbenko-Germanov[72] suggest oxidation of americium to americium(V) in 50 percent carbonate solution with ozone, hypochlorite, or peroxydisulfate ion. Americium precipitates from solution as the double carbonate salt. When tracer americium is present the

Figure 25. Separation of americium and curium by selective elution from a Dowex-50 cation exchange resin column with alpha-hydroxy-isobutyric acid at pH 4.02.

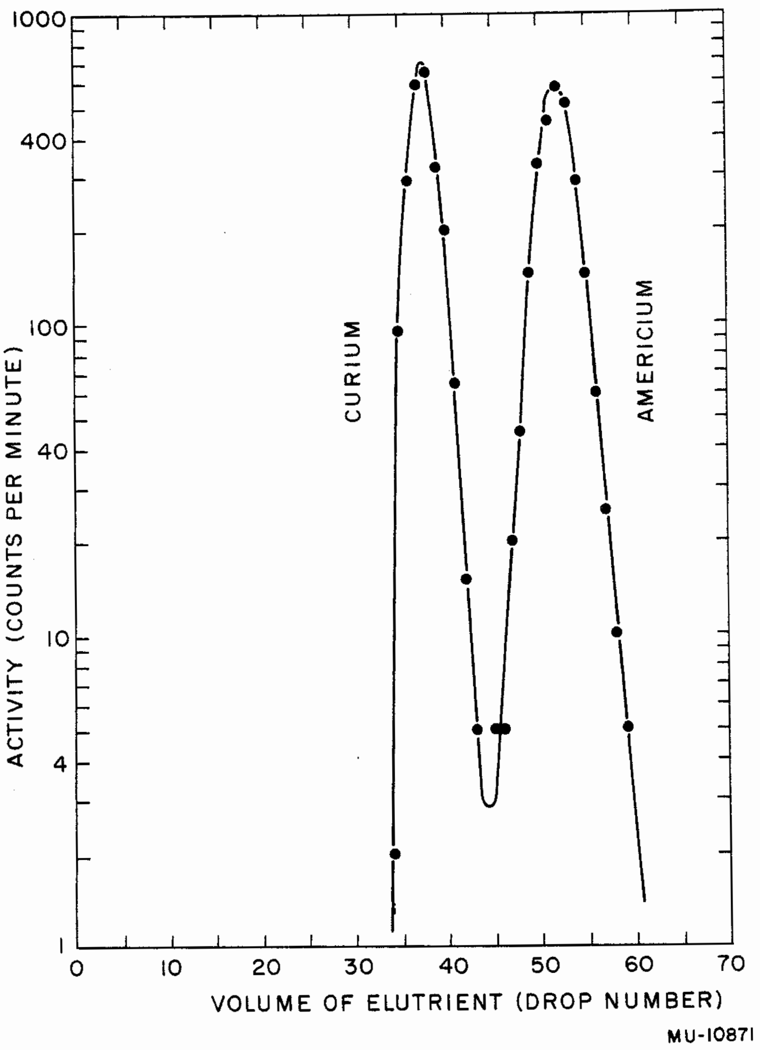
1000
400
100
40
10
4
1
ACTIVITY (COUNTS PER MINUTE)
CURIUM
AMERICIUM
0
10
20
30
40
50
60
70
VOLUME OF ELUTRIENT (DROP NUMBER)
MU-10871

Figure 25

compound potassium uranyl carbonate can be precipitated as a carrier.

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[69] D. F. Peppard, P. R. Gray, and M. M. Markus, J. Am. Chem. Soc. 75, 6063 (1953).

[70] S. E. Stephanou and R. A. Penneman, J. Am. Chem. Soc. 74, 3701 (1952).

[71] S. R. Gunn, Ph.D. Thesis, University of California Radiation Laboratory Declassified Report UCRL-2541.

[72] G. N. Yakovlev and D. S. Gorbenko-Germanov, Paper P/677, "Proceedings of the Geneva Conference--Peaceful Uses of Atomic Energy," August 1955, United Nations.

The absorption spectrum of curium solutions has no structure in the visible region, and although it absorbs heavily in the ultraviolet it shows no sharp absorption bands. Hence curium solutions cannot be analyzed by the spectrophotometric methods so useful for the other actinide elements. Analysis is done by measuring the alpha particle emission rate (often with the refinement of alpha particle energy determination) or by spectrographic analysis for impurities.

49. Anhydrous compounds of curium. The number of well characterized anhydrous curium compounds is quite small. The metal has been prepared repeatedly on the microgram scale by precipitating curium trifluoride from aqueous solution, drying it, and reducing it in a beryllia crucible in a vacuum system with barium vapor at 1275° C.[73] Conditions are critical for securing a good agglomerate. The metal is silvery and shiny and about as malleable as plutonium metal. Under nitrogen it retains its luster for several hours, then slowly tarnishes. The energy of alpha decay keeps the metal temperature substantially above that of the surroundings. An estimate was made of the density of a spheroidal piece of metal by weighing it and estimating its volume. The unexpectedly low value of approximately 7 may indicate a void.

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[73] J. C. Wallman, W. W. T. Crane, and B. B. Cunningham, J. Am. Chem. Soc. 73, 493 (1951).

X-ray studies of curium (Cm^{242}) oxide samples have two limiting difficulties; namely, fogging of the film from the Cm^{242} radiations and destruction of the crystal lattice by alpha recoil effects. Nevertheless some positive measurements have been made. These have been supplemented by measurements made with the longer lived Cm^{244}. A white sesquioxide Cm_2O_3 and a black dioxide CmO_2 have been identified.[74] This is the first clear evidence for a higher oxidation state for curium.

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[74] L. B. Asprey, F. H. Ellinger, S. Fried, W. H. Zachariasen, J. Am. Chem. Soc. 77, 1707 (1955).

Feay, Cunningham, and Conway[75] have examined the absorption spectrum of solid CmF_3 and of solid GdF_3 on a 21-foot spectrograph. Marked similarities in the spectra of these homologous element compounds were found. The prominent lines are compared in Table 23. Below 2850 Å no absorption was found in either compound. These similarities support the belief that the electronic configuration of curium is $5f^7$ analogous to the $4f^7$ structure of gadolinium.

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[75] D. C. Feay, B. B. Cunningham, and J. Conway, unpublished work; see D. C. Feay, Ph.D. thesis, University of California Radiation Laboratory Unclassified Report UCRL-2547 (1954).

Table 23. Prominent Lines in the Ultraviolet Absorption Spectra of Solid CmF_3 and GdF_3.

CmF_3 λ, Å	Relative Intensity	GdF_3 λ, Å	Relative Intensity
2826	2	2834	4
2774	10	2759	10
2680	6	2666	4
2368	4	2334	4

On an absolute scale absorption by CmF_3 is much stronger than that by GdF_3.

The magnetic susceptibility of curium trifluoride has been determined at two temperatures using samples of only about 25 micrograms.[75a] The molar susceptibility (in c.g.s units x 10^6) is 22,500 ± 4000 at 295° K and 58,000 ± 6000 at 77° K. The value 22,500 is in reasonably good agreement with the theoretical value, 26,000, for 295° K, if one assumes an electron configuration $5f^7$ for the ground state configuration.

[75a] W. W. T. Crane, B. B. Cunningham, and J. C. Wallmann, University of California Radiation Laboratory Unclassified Report UCRL-846 (1950).

The wavelengths of the most prominent lines in the arc and spark spectra of curium were measured[76] using one microgram samples. The region from 2516 to 5000 Å was covered and over 200 lines were recorded. The isotope shift was observed in curium optical spectra when a mixture of Cm^{242} and Cm^{244} was run; the shift was seen in 148 lines out of the 182 lines recorded.[77] The magnitude of the shift ranged up to 0.131 cm^{-1}.

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[76] J. G. Conway, M. F. Moore, and W. W. T. Crane, J. Am. Chem. Soc. 73, 1308 (1951).

[77] J. G. Conway and R. D. McLaughlin, University of California Radiation Laboratory Report UCRL-3037 (1955); J. Opt. Soc. Am. 46 (1956).

V. BERKELIUM (ELEMENT 97)

50. Discovery of berkelium - summary of known isotopes. Some years elapsed between the identification of americium and curium and the first proof of the synthesis of element 97. This time was needed to overcome the experimental difficulties in working with highly radioactive cyclotron target materials, in improving the necessary ion exchange chemical techniques and in deriving correlations of heavy element nuclear properties to permit prediction of the properties of expected isotopes.

In December 1949 an isotope of the element 97 was synthesized and identified by Thompson, Ghiorso, and Seaborg.[78] The isotope of mass number 243 was made by the (α, 2n) reaction in the Berkeley 60-inch cyclotron using milligram amounts of Am^{241} as target material and bombarding with 35-Mev helium ions. Element 97 is a chemical homologue of the rare earth terbium which was named after the town of Ytterby, Sweden; hence the name berkelium (symbol Bk) was proposed in honor of the city of Berkeley.

The isotope, Bk^{243}, decays primarily by orbital electron capture with a half-life of 4.6 hours. Branching decay by alpha particle emission occurs to the extent of about 0.1 percent and in this decay three groups of alpha particles of energies 6.72, 6.55, and 6.20-Mev are emitted.

A number of other isotopes of berkelium have been made by cyclotron bombardments of americium or curium targets or by intense and prolonged neutron irradiation of plutonium or americium samples. The principal decay characteristics of these isotopes are listed in Table 24 and Figure 26. The most intense sources of berkelium have been made in nuclear reactors; samples of berkelium of 10^8 disintegrations per min. of Bk^{249} (approximately .025 micrograms) have been isolated and considerably larger amounts can be made. All chemical studies to date have been carried out on a tracer scale, but weighable amounts of berkelium can be prepared by multiple neutron capture reactions such as the following:

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[78] S. G. Thompson, A. Ghiorso, and G. T. Seaborg, Phys. Rev. 80, 781 (1950).

$$\mathrm{Pu}^{239}(n,\gamma)\mathrm{Pu}^{240}(n,\gamma)\mathrm{Pu}^{241}(n,\gamma)\mathrm{Pu}^{242}(n,\gamma\mathrm{Pu}^{243}\xrightarrow[5.0\ \mathrm{hr.}]{\beta^-}\mathrm{Am}^{243}(n,\gamma)\mathrm{Am}^{244}$$

$$\xrightarrow{\beta^-}\mathrm{Cm}^{244}(n,\gamma)\mathrm{Cm}^{245}(n,\gamma)\mathrm{Cm}^{246}(n,\gamma)\mathrm{Cm}^{247}(n,\gamma)\mathrm{Cm}^{248}(n,\gamma)\mathrm{Cm}^{249}$$

$$\xrightarrow{\beta^-}\mathrm{Bk}^{249}. \qquad (47.1)$$

Alternatively one could carry out this sequence in two stages by isolating and chemically purifying the curium fraction then reinserting it in the reactor for the final conversion to berkelium.

Figure 26. Decay schemes of berkelium isotopes.

With larger amounts of Bk^{249} or preferably of 7000-year Bk^{247} it will be possible to characterize many chemical compounds and to measure important thermodynamic quantities with accuracy.

51. Chemical properties of berkelium. The chemical properties of the tripositive solution state of berkelium are markedly similar to the neighboring tripositive actinide element ions and to the tripositive rare-earths. Since rare-earth fission products and neighboring actinide elements are always present when berkelium is produced, its separation from these elements is of considerable importance. The ion exchange elution technique is of primary importance. To separate berkelium from Am^{241} cyclotron targets, Thompson, Ghiorso, and Seaborg[78] proceeded as follows:

The bombarded Am^{241} was dissolved in nitric acid, precipitated as hydroxide (carrying the berkelium and the rare-earths), separated and redissolved in 0.1 molar nitric acid. Ammonium peroxydisulfate was added and the solution heated to 75° C for 1-1/2 hrs. The major portion of the americium was oxidized to fluoride-soluble americium(VI). Removing this bulk of material improves the sharpness and speed of later ion exchange separations. The residual americium(III) was precipitated as the trifluoride to serve as a carrier for berkelium, curium and rare earth fission products. The fluoride precipitate was methathesized to the hydroxide, washed, and dissolved in 0.5 molar perchloric acid. The mixture of radioactivities was absorbed on the top of a 20-cm length by 2-millimeter diameter column of Dowex-50 cation resin. This column was operated at 87° C. The elution was performed by passing 0.25 molar ammonium citrate buffered with citric acid to pH 3.5 through the column at the rate of one drop every two

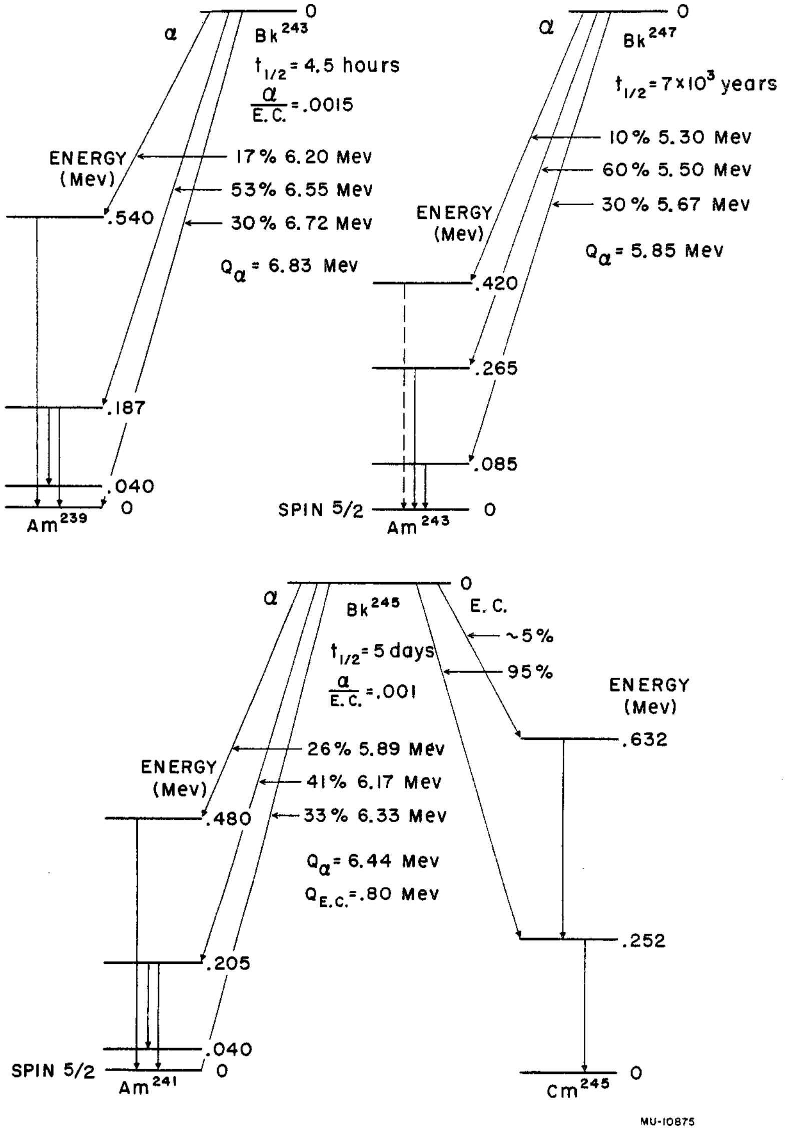
α
0
Bk^{243}
$t_{1/2}$ = 4.5 hours
$\frac{\alpha}{E.C.}$ = .0015
ENERGY (Mev)
17% 6.20 Mev
53% 6.55 Mev
30% 6.72 Mev
Q_α = 6.83 Mev
.540
.187
.040
0
Am^{239}
α
0
Bk^{247}
$t_{1/2}$ = 7×10^3 years
10% 5.30 Mev
60% 5.50 Mev
30% 5.67 Mev
ENERGY (Mev)
Q_α = 5.85 Mev
.420
.265
.085
SPIN 5/2
0
Am^{243}
α
0
Bk^{245}
E. C.
~5%
$t_{1/2}$ = 5 days
95%
$\frac{\alpha}{E.C.}$ = .001
ENERGY (Mev)
.632
26% 5.89 Mev
41% 6.17 Mev
ENERGY (Mev)
33% 6.33 Mev
.480
Q_α = 6.44 Mev
$Q_{E.C.}$ = .80 Mev
.252
.205
.040
SPIN 5/2
0
Am^{241}
0
Cm^{245}
MU-10875

Figure 26

Table 24. Isotopes of Berkelium*

Isotope and Half-Life	Type of Decay	Energy (Mev)	Method of Production	Disintegration Energies (Mev) †
Bk^{243} 4.5 h	EC 99^{+}% α 0.15% (Ref. 1) γ	6.72(30%) 6.55(53%) 6.20(17%) .740, .840, .960 following EC .147, .187, .540 following α	Am^{241} α-2n Cm^{242}d-n Am^{243}α-4n	Q_{EC}=1.54 (calc.) Q_{α}=6.83
Bk^{244} 4.4 h(Ref. 2)	EC α 6 x 10^{-5}% (Ref. 2) γ	6.66(100%)(Ref. 2) .900, 1.060, 1.160, 1.230, 1.370, 1.500, 1.720(Ref. 2)	Am^{241}α-n Am^{243}α-3n	Q_{EC}=2.32(est.) Q_{α}=6.77
Bk^{245} 5.0 d	EC 99^{+}% α 0.1% γ	5.89(26%), 6.17(41%) 6.33(33%) (Ref. 2) .252, .380(Ref. 2)following EC .165, .205, .480 following α	Cm^{244}d-n Am^{243}α-2n	Q_{EC}=0.80 (calc.) Q_{α}=6.44
Bk^{246} 1.9 d(Ref. 2)	EC γ	.145, .800, .980, 1.030, 1.130 (Ref. 2)	Am^{243}α-n	Q_{EC}=1.34 (est.) Q_{α}=6.15(est.)
Bk^{247} 7 x 10^{3}y(Ref.2)	α γ	5.67(30%), 5.50(60%) 5.30(10%) (Ref. 2) .085, .265, .420 (?) following α	Cm^{244}α-n daughter Cf^{247}	Q_{α} =5.85 Q_{EC}=0.04(est.)
Bk^{248} 18 h(Ref.2)	β^-(75%) EC(25%) $\frac{K}{L+M} \sim 1$	.670	Pu^{239} multiple n capture Bk^{247}n-γ	Q_{EC}=0.65(est.) Q_{β^-}=0.66 Q_{α} =5.52(calc.)
Bk^{249} 270 d(Ref. 3) 290 d(Ref. 4) 6 x 10^{8}y spon. fiss.	β^- α 10^{-3}% (Ref. 4) γ	.100 (Ref. 2) 5.40(94%), 5.08(6%) (Ref. 2) .320 with α	Pu^{239} multiple n capture	Q_{β} =0.10 Q_{α} =5.51

Isotope and Half-Life	Type of Decay	Energy (Mev)	Method of Production	Disintegration Energies (Mev) †
Bk^{250} 3.13 h (Ref. 5)	β^- γ	0.9, 1.9(Ref. 5) 0.9(Ref. 5)	Bk^{249}n-γ(Ref. 5)	Q_β = 1.90 Q_α = 5.73(calc.)

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* For references to original data not given specifically here, refer to Hollander, Perlman and Seaborg, "Table of Isotopes," Rev. of Mod. Physics, 25, 469 (1953) and to the compilations of the Nuclear Data Group, National Research Council.

1. E. K. Hulet, Ph. D. Thesis, University of California Radiation Laboratory Report, UCRL-2283 (1953).
2. A. Chetham-Strode, Ph. D. Thesis, University of California Radiation Laboratory Report, UCRL-3322 (1956).
3. S.G. Thompson, et al. Phys. Rev. 93, 908 (1954).
4. L.B. Magnusson, et al. Phys. Rev. 96, 1576 (1954).
5. A. Ghiorso, et al. Phys. Rev. 94, 1081 (1954).

† Revised values from R. A. Glass, S. G. Thompson and G. T. Seaborg, J. Inorg. and Nucl. Chem. 1, 3 (1955).

minutes. Element 97 was found in drops 40 through 45 and for comparison curium was collected in drops 65 to 70. In order to separate element 97 from residual rare-earth contaminants (principally terbium and gadolinium) the berkelium fraction was adsorbed on a second column of Dowex-50 resin of approximately 7-cm length. Elution with 13 molar hydrochloric acid removed the berkelium well ahead of rare earth contaminants.

An interesting aspect of the elution behavior of berkelium is the striking similarity in the spacing of the elution peaks in the sequence americium - curium - berkelium - californium as compared to europium - gadolinium - terbium - dysprosium. The spacings are shown in Figure 27. The gap in the center of the curves is probably a reflection of a break in the change of ionic radius which occurs in both series just after the half-filling of the 4f or 5f electron shell. The behavior of berkelium in this regard was predicted by Boyd.[79]

Figure 27. Elution curves for the actinide element group americium - curium - berkelium - californium as compared to the homologous elements europium - gadolinium - terbium - dysprosium.

Recent studies in ion exchange elution have shown that buffered lactic acid[80, 81] and particularly buffered α-hydroxy-isobutyric acid[82, 83] are superior to ammonium citrate. (See Figure 31, Section 55).

The elution of the berkelium ahead of the rare-earths when 13 molar hydrochloric acid is used as eluting agent indicates that berkelium forms stronger chloride complexes than the lanthanide ions. More striking evidence for this is the fact that berkelium can be adsorbed from 13 molar hydrochloric acid onto a column of anion-exchange resin such as Dowex-1. This adsorption is weak and the berkelium can readily be desorbed with 13 molar hydrochloric acid, but there is an appreciable delay after the elution of americium and curium. (See Figure 30, Section 55). Stronger adsorption on anion resins is achieved from thiocyanate solution.[84]

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[79] G. E. Boyd, U. S. Atomic Energy Commission Report MDDC 840 (April 16, 1947).

[80] R. A. Glass, J. Am. Chem. Soc. 77, 807 (1955).

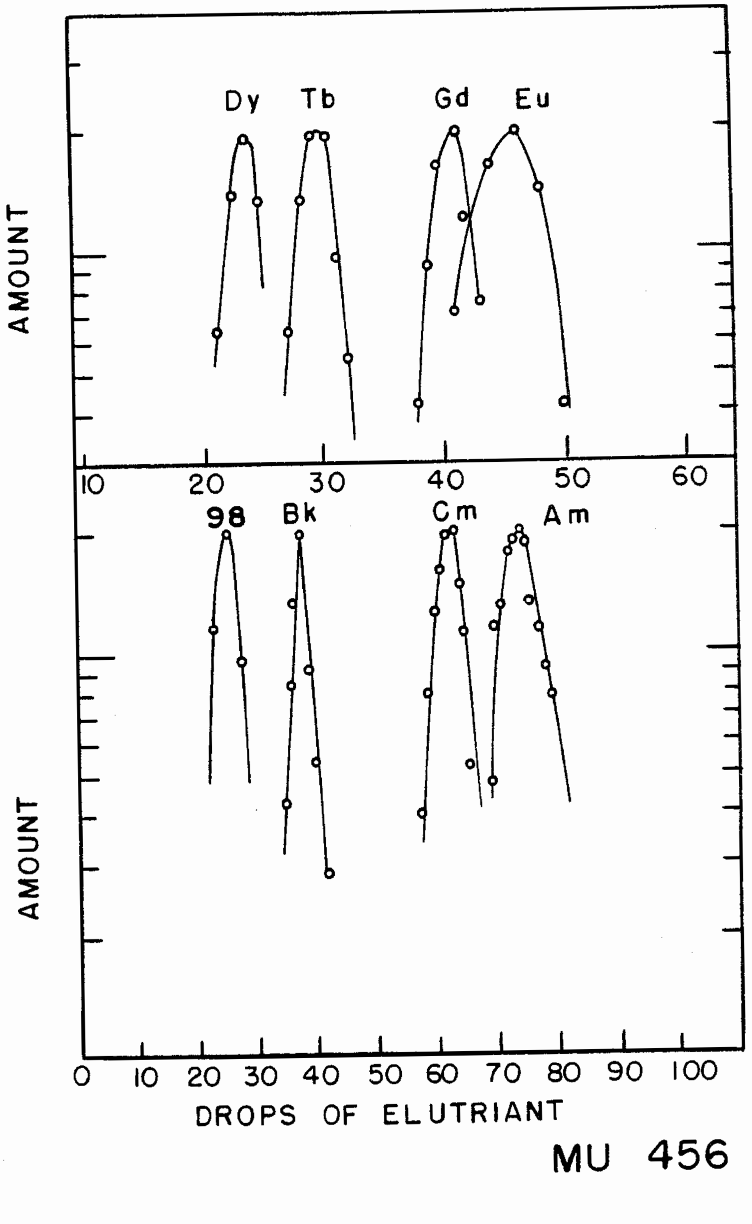
Dy
Tb
Gd
Eu
AMOUNT
10
20
30
40
50
60
98
Bk
Cm
Am
AMOUNT
0
10
20
30
40
50
60
70
80
90
100
DROPS OF ELUTRIANT
MU 456

Figure 27

[81] L. Wish, E. C. Freiling, and L. R. Bunney, J. Am. Chem. Soc. 76, 3444 (1954).

[82] G. R. Choppin, B. G. Harvey, and S. G. Thompson, University of California Radiation Laboratory Report UCRL-3022; J. Inorg and Nucl. Chem. 2, (1956)

[83] G. R. Choppin and R. J. Silva, University of California Radiation Laboratory Report UCRL-3265, 1956.

[84] J. Surls, thesis, University of California Radiation Laboratory UCRL-3209 (1955).

The coprecipitation behavior of tripositive berkelium is identical with that of other actinide elements and coprecipitation is observed with such typical carrier compounds as lanthanum fluoride or lanthanum hydroxide. The nitrate, chloride, sulfate, bromide, perchlorate, and sulfide salts are apparently soluble. Berkelium can be extracted readily into benzene as a chelate complex of α-thenoyltrifluoroacetone[85] (T.TA). At pH 3.4 the extraction of berkelium and californium is roughly a factor of ten greater than that of americium and curium.

It was anticipated by Seaborg[86] that element 97 as ekaterbium in the actinide transition series would possess a tetrapositive oxidation state. Berkelium(IV) has the half-completed shell configuration $5f^7$ which has a special stability. Such an oxidation state has indeed been found[87] by tracer experiments in which treatment with bromate ion, dichromate ion, or ceric ion caused oxidation of berkelium to a form coprecipitated with zirconium phosphate or zirconium iodate, compounds which are rather specific carriers for tetrapositive ions. The oxidation potential of the berkelium (III) - berkelium(IV) couple is about -1.6 volts.[87]

It may be expected that milligram quantities of berkelium in the form of 7000-year Bk^{247} will eventually be available and that the chemistry of the element including characterization of solid compounds and measurement of thermodynamic quantities will be at least as extensive as is presently the case for americium.

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[85] L. B. Magnussen and M. L. Anderson, J. Am. Chem. Soc. 76, 6207 (1954)

[86] G. T. Seaborg, Nucleonics 5 (5):16(1949); Paper 22.1 N. N. E. S. Vol. 14B "The Transuranium Elements" 1949.

[87] S. G. Thompson, B. B. Cunningham, and G. T. Seaborg, J. Am. Chem. Soc. 72, 2798 (1950)

VI. CALIFORNIUM (ELEMENT 98)

52. Discovery of californium - summary of known isotopes. Following within two months the first successful identification of berkelium, the synthesis and identification of an isotope of element 98 was carried out by Thompson, Street, Ghiorso, and Seaborg[88] in February 1950. This first isotope of element 98, tentatively assigned the mass number 244, was produced when microgram amounts of Cm^{242} (about 10^{11} alpha disintegrations per minute) were bombarded with 35-Mev helium ions in the 60-inch cyclotron of the University of California at Berkeley. The isotope decayed partly by the emission of alpha particles of energy 7.1-Mev and partly by electron capture with a half-life of 45 min. At the time of the first experiments the tentative mass assginment was 244. Later it was established that the correct mass number was 245. Many serious experimental problems had to be overcome in bombarding safely such a highly radioactive target and in swiftly making complete chemical separation of the minute amount of the new element from the chemically very similar heavy elements and the prominent rare-earth fission product activity.

The name californium, symbol Cf, was chosen in honor of the university and the state where the work was done. Californium is the eighth member of the actinide series and is the homologue of dysprosium of the rare-earth series.

A number of californium isotopes ranging in mass from 244 to 254 have been synthesized. Data on californium isotopes are summarized in Table 25. Decay schemes are shown in Figure 28. A number of these have been made by (α, xn) reactions on curium targets. Another method for their production is the bombardment of targets of lower atomic number with accelerated heavy ions.[89, 90]

Figure 28. Decay schemes of californium isotopes.

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[88] S. G. Thompson, K. Street, Jr., A. Ghiorso, and G. T. Seaborg, Phys. Rev. 80, 790 (1950).

[89] A. Ghiorso, S. G. Thompson, K. Street, Jr., and G. T. Seaborg, Phys. Rev. 81, 154 (1951).

[90] A. Ghiorso, G. B. Rossi, B. G. Harvey, and S. G. Thompson, Phys. Rev. 93, 257 (1954).

In this manner Cf^{244} and Cf^{246} have been produced by bombardment of uranium targets with carbon ions accelerated to approximately 120 Mev; similarly Cf^{245}, Cf^{246}, Cf^{247}, and Cf^{248} have been produced by the bombardment of uranium targets with nitrogen ions accelerated to 140 Mev. A sample reaction of this type is:

$$U^{238} + {}_6C^{12} \longrightarrow Cf^{246} + 4\,{}_0n^1. \qquad (49.1)$$

By far the best method for the production of larger amounts of californium is the bombardment of gram or larger amounts of heavy element isotopes such as Pu^{239} in modern high flux reactors. Successive neutron capture reactions proceeding through a sequence such as the following can convert substantial amounts of lighter mass material into high mass californium isotopes. Considerable material is lost through fission in the first few steps, but beyond this point a considerable fraction of the cross-section goes into capture reactions.

$$Pu^{239}(n,\gamma)Pu^{240}(n,\gamma)Pu^{241}(n,\gamma)Pu^{242}(n,\gamma)Pu^{243} \xrightarrow[5.0\text{ hr}]{\beta^-} Am^{243}(n,\gamma)$$

$$Am^{244} \xrightarrow[26\text{ min.}]{\beta^-} Cm^{244}(n,\gamma)Cm^{245}(n,\gamma)Cm^{246}(n,\gamma)Cm^{247}(n,\gamma)Cm^{248}$$

$$(n,\gamma)Cm^{249} \xrightarrow[\text{short}]{\beta^-} Bk^{249}(n,\gamma)Bk^{250} \xrightarrow[3.13\text{ hr.}]{\beta^-} Cf^{250}(n,\gamma)Cf^{251}(n,\gamma)$$

$$Cf^{252}(n,\gamma)Cf^{253}(n,\gamma)Cf^{254}.$$

Experiments with californium fractions isolated from highly irradiated plutonium samples (nvt of the order of 10^{22}) have revealed substantial new information[91, 92] on heavier isotopes of the element. The isotopic composition[91] of the californium fraction from such an irradiation was determined mass spectrographically to be 4.3 percent Cf^{249}, 49 percent Cf^{250}, 11 percent Cf^{251}, and 36 percent Cf^{252}. Data on these isotopes are given in Table 26.

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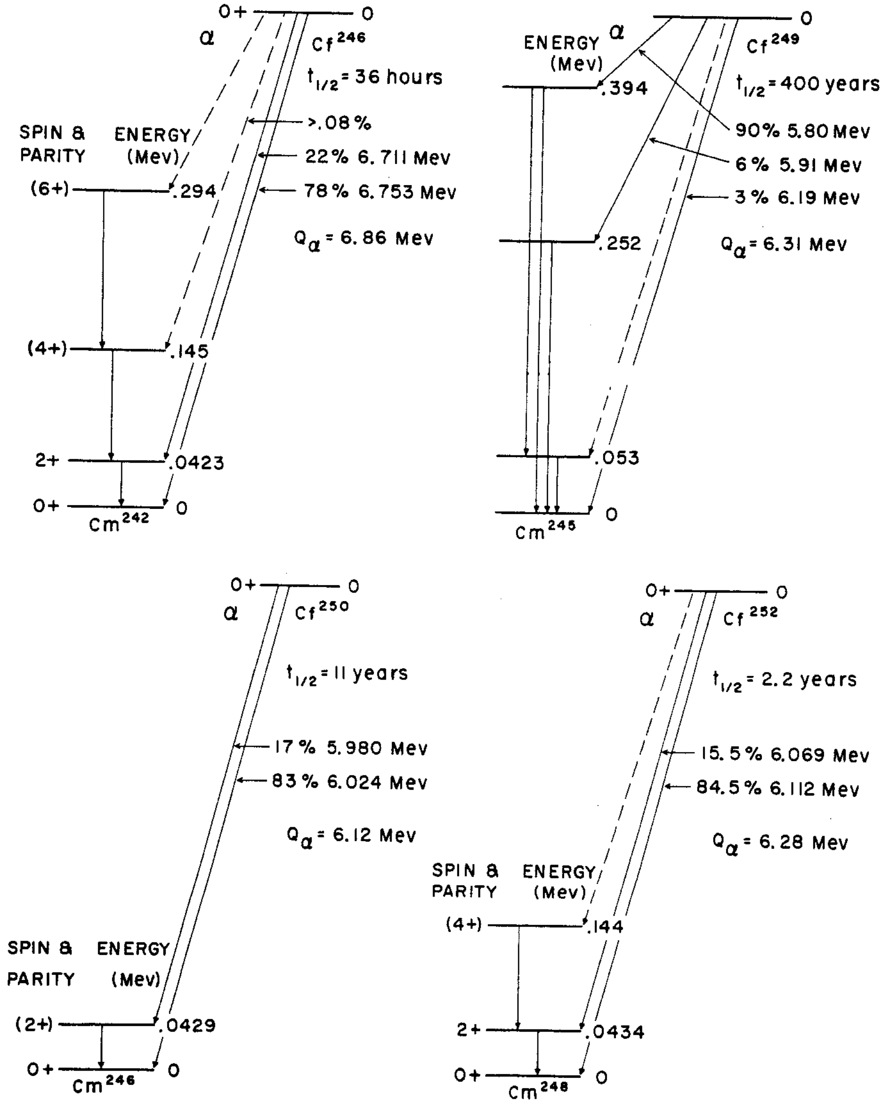
[91] H. Diamond et al, Phys. Rev. 94, 1083 (1954); L. B. Magnusson et al, Phys. Rev. 96, 1576 (1954).

[92] A. Ghiorso, S. G. Thompson, G. R. Choppin, and B. G. Harvey, Phys. Rev. 94, 1081 (1954).



0+
0
α
Cf^{246}
$t_{1/2}$ = 36 hours
>.08%
22% 6.711 Mev
78% 6.753 Mev
Q_α = 6.86 Mev
SPIN & PARITY
ENERGY (Mev)
(6+)
.294
(4+)
.145
2+
.0423
0+
0
Cm^{242}
0
ENERGY (Mev)
α
Cf^{249}
$t_{1/2}$ = 400 years
.394
90% 5.80 Mev
6% 5.91 Mev
3% 6.19 Mev
.252
Q_α = 6.31 Mev
.053
0
Cm^{245}
0+
0
α
Cf^{250}
$t_{1/2}$ = 11 years
17% 5.980 Mev
83% 6.024 Mev
Q_α = 6.12 Mev
SPIN & PARITY
ENERGY (Mev)
(2+)
.0429
0+
0
Cm^{246}
0+
0
α
Cf^{252}
$t_{1/2}$ = 2.2 years
15.5% 6.069 Mev
84.5% 6.112 Mev
Q_α = 6.28 Mev
SPIN & PARITY
ENERGY (Mev)
(4+)
.144
2+
.0434
0+
0
Cm^{248}

Figure 28

Eventually it will be possible to prepare the isotopes Cf^{249}, Cf^{250}, Cf^{251}, and Cf^{252} in weighable amounts so that the chemical properties of californium can be investigated in considerably more detail.

The spontaneous fission characteristics of californium are quite important and will be summarized later in this report.

b. The Chemistry of Californium

53. Chemical properties of californium.[88, 93, 94] The only oxidation state known is the tripositive state. The californium(III) - californium(IV) couple is expected to be much more negative than -1.6 volts which would make californium(IV) unobtainable in aqueous solution. There is a possibility that californium(V) may be found in the future because of the special stability of the $5f^7$ configuration. Determined efforts have been made to oxidize it with such powerful oxidants as peroxydisulfate and bismuthate ions without success. So far as is known the chemistry of californium is nearly identical with that of the other tripositive actinide ions. It can be coprecipitated with such typical carriers as lanthanum fluoride and lanthanum oxalate. The nitrate, sulfate, bromide, chloride, iodide, sulfide and perchlorate appear to be soluble. The principal method of chemical purification is ion exchange. Californium adsorbs on cation exchange resin columns and can be eluted ahead of berkelium with buffered citrate, lactate, alpha-hydroxy-isobutyrate and similar eluting agents. (See for example, Figure 31, Section 55). It can be eluted with 13 molar hydrochloric acid from cation exchange columns; it elutes just ahead of berkelium and well ahead of the first rare earth element. (See Figure 30, Section 55). Californium forms anionic chloride complexes in 13 molar hydrochloric acid and can be adsorbed on an anion resin column. The californium is readily eluted with more 13 molar hydrochloric acid but with sufficient delay to effect a separation from berkelium, americium, and curium, and, of course, the rare-earth elements which do not adsorb on the column at all. (See for example, Figure 30, Section 55).

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[93] K. Street, Jr., S. G. Thompson, and G. T. Seaborg, J. Am. Chem. Soc. 72, 4832 (1950).

[94] S. G. Thompson, B. G. Harvey, G. R. Choppin, and G. T. Seaborg, J. Am. Chem. Soc. 76, 6229 (1954).

Table 25 Isotopes of Californium*

Isotope and Half-Life	Type of Decay	Energy(Mev)	Method of Production	Disintegration** Energies(Mev)
Cf^{244} 25 m(Ref. 1)	α	7.17(Ref. 2)	U^{238} C-6n Cm^{242}α-2n	Q_α =7.29 Q_{EC} =0.60(est.)
Cf^{245} 44 min (mass reassignment Ref. 1)	EC(66%) α(34%)	7.11	Cm^{242}α-n Cm^{244}α-3n	Q_{EC} =1.64(est.) Q_α =7.23
Cf^{246} 35.7 h α 2.1×10^3y spon. fiss.	α γ	6.711(22%), 6.753(78%) (Ref. 3) .044(Ref. 3), .097±.0 03 (1.3×10^{-4}), .149±.005(3.4×10^{-5}) (Ref. 12)	Cm^{244}α-2n U^{238} C-4n Cm^{243}α-n U^{238}N-p5n	Q_α =6.86 Q_{EC} =0.12(est.)
Cf^{247}(Ref. 4) 2.4 h(Ref. 2)	EC γ	 .285, .490(Ref. 2)	Cm^{244}α-n(Ref. 2) U^{238}N-p4n(Ref. 4)	Q_{EC} =0.77(est.) Q_α =6.62(est.)
Cf^{248}(Ref. 4) 250 d 7×10^3y spon. fiss.	α β stable	6.26(Ref. 5)	U^{238}N-p3n(Ref. 4) Cm^{245}α-n(Ref. 5)	Q_α =6.36
Cf^{249} 400 y α(Ref. 6) 470 y α(Ref. 7) 1.5×10^9 y spon. fiss.	 α β stable γ	 5.82(90%)(Ref. 6)6.190(3%) 5.91(6%)(Ref. 11) .25, .053, .265(?)	 daughter Bk^{249}	 Q_α =6.31
Cf^{250} 12 y α(Ref. 6) 10 y α(Ref. 7) 1.5×10^4y spon. fiss.	α β stable γ	5.980(17%), 6.024(83%) .0428(.014%)	daughter Bk^{250} Bk^{249}n-γβ	Q_α =6.12

Isotope and Half-Life	Type of Decay	Energy(Mev)	Method of Production	Disintegration Energies(Mev)**
Cf^{251} ≫18 d (Ref.7)	β stable		Pu^{239} multiple n capture	$Q_\alpha = 6.32$(est.)
Cf^{252} 2.2 y α(Ref. 7) 66 y spon. fiss.	α β stable γ	6.112(84.5%), 6.069(15.5%) (Ref. 8) .0434, .100(Ref. 11)	Pu^{239} multiple n capture	$Q_\alpha = 6.28$
Cf^{253} 20d(Ref. 6) 18 d(Ref. 7)	β^-		Pu^{239} multiple n capture	$Q_{\beta^-} = 0.54$(est.) $Q_\alpha = 6.20$(est.)
Cf^{254} 85 d(Ref. 9) 60 d(Ref. 10)	spon. fiss. β stable		daughter E^{254}	$Q = 6.03$(est.)

* For references to original data not given specifically here, refer to Hollander, Perlman and Seaborg "Table of Isotopes," Rev. of Mod. Physics 25, 469 (1953) and to the compilations of the Nuclear Data Group, National Research Council.

** Revised values from Glass, Thompson and Seaborg 1 3 1955.

1. A. Chetham-Strode, et. al. University of California Radiation Laboratory Report UCRL-3219(Dec. 1955).
2. A. Chetham-Strode, Ph.D. Thesis, University of California Radiation Laboratory Report UCRL-3322(1956).
3. J. P. Hummel et. al., Phys. Rev. 98, 22 (1955).
4. A. Ghiorso et. al., Phys. Rev. 93, 257 (1954).
5. E. K. Hulet, et. al., Phys. Rev. 95, 1702 (1954).
6. A. Ghiorso et. al., Phys. Rev. 94, 1081 (1954).
7. L. B. Magnusson et. al., Phys. Rev. 96, 1576 (1954).
8. I. Perlman, et. al., reported in University of California Radiation Laboratory Reports UCRL-2932 (March 1955) and UCRL-3068 (July 1955).
9. B. G. Harvey et. al., Phys. Rev. 99, 337 (1955).
10. W. C. Bentley, et. al. Paper P 809 "Peaceful Uses of Atomic Energy - Proceedings of the Geneva Conference" United Nations, August, 1955.
11. F. S. Stephens Ph.D. Thesis, University of California Radiation Laboratory Report UCRL-2970 (April 1955).
12. I. Perlman et. al., University of California Radiation Laboratory Report UCRL-3068 p. 37 (July, 1955).

Our present knowledge of californium chemistry has all been obtained with tracer amounts. Later studies with weighable amounts should provide considerable quantitative information.

VII. EINSTEINIUM (ELEMENT 99)

54. Discovery of einsteinium - summary of known isotopes. The first identification of an isotope of element 99 and of element 100 came about as the result of careful analysis of heavy element samples from the "Mike" thermonuclear explosion staged by the Los Alamos Scientific Laboratory in November 1952. The uranium in this device was subjected to a very intense instantaneous neutron flux which by multiple neutron capture reactions of a very high order gave rise to very heavy uranium isotopes which rapidly decayed by beta emission into previously uninvestigated heavy isotopes of neptunium, plutonium, americium, curium, berkelium, californium, and of the elements 99 and 100. Three teams of nuclear chemists[95] working at the University of California Radiation Laboratory, the Argonne National Laboratory, and the Los Alamos Scientific Laboratory contributed to the chemical isolation and identification of the new elements in December 1952. The scientists involved were A. Ghiorso, S. G. Thompson, G. H. Higgins, and G. T. Seaborg of the University of California, M. H. Studier, P. R. Fields, S. M. Fried, H. Diamond, J. F. Mech, G. L. Pyle, J. R. Huizenga, A. Hirsch, and W. M. Manning of the Argonne National Laboratory, and C. I. Browne, H. L. Smith, and R. W. Spence of the Los Alamos Laboratory.

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[95] Phys. Rev. 99, 1048 (1955).

The names which have been suggested and accepted for these elements are einsteinium (symbol E) after Albert Einstein, for element 99 and fermium (symbol Fm) after Enrico Fermi, for element 100.

Einsteinium and fermium are actinide elements with chemical properties very similar to other actinide elements in the tripositive state. Hence, as in the identification of berkelium and californium, the ion exchange elution technique played a prominent role in the purification and identification. Rare-earth contaminants were removed by adsorbing the contaminated heavy element fractions on Dowex-50 cation resin and eluting with 13 molar hydrochloric acid. The partially purified heavy element fraction was then adsorbed on another column of Dowex-50 resin and eluted carefully with ammonium citrate solution to effect separation of the individual actinide elements. These experiments showed the elution of a 6.6 Mev alpha activity ahead of the element californium and in the expected eka-holmium (element 99) position. Also a new 7.1 Mev alpha activity was found to elute in the eka-erbium (element 100) position. The conclusions from the detailed experiments were the following: An appreciable amount of U^{253} had formed in the initial nuclear explosion. This rapidly decayed by a chain of short-lived beta emissions to Cf^{253} which decayed by beta emission with a half-life of approximately 20 days to E^{253} which decayed with the with the emission of 6.6 Mev alpha particles with a half-life of about 20 days. Similarly an appreciable amount of U^{255} had formed instantaneously and had decayed via a long beta-emitter chain to E^{255} which decayed by beta emission with a half-life of approximately 30 days to Fm^{255} which decayed by the emission of 7.1 Mev alpha particles with a half-life of approximately 16 hrs.

The bombardment of uranium targets[96] with nitrogen ions accelerated to more than 100 Mev energy in a cyclotron has produced small amounts of short-lived activities tentatively assigned to E^{246} and E^{247}.

By neutron irradiation of Pu^{239} in the high flux Materials Testing Reactor in Idaho for extended periods of time (integrated flux between 10^{21} and 10^{22} neutrons) it has been possible to produce californium isotopes containing substantial percentages of higher mass isotopes. (See Section 52); by prolonged reirradiation the mass of californium isotopes was increased until the beta emitter Cf^{253} was reached. The daughter isotope, 20-day E^{253} was isolated from these samples.[97, 98]

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[96] A. Ghiorso, G. B. Rossi, B. G. Harvey, and S. G. Thompson, Phys. Rev. 93, 257 (1955).

[97] S. G. Thompson, A. Ghiorso, B. G. Harvey, and G. R. Choppin, Phys. Rev. 93, 908 (1954).

[98] M. H. Studier, et al, Phys. Rev. 93, 1428 (1954).

Irradiation of E^{253} with neutrons results in the production of the isomer pair E^{254m},[99-101] and E^{254}. E^{254m} decays by beta emission with a half-life of 36 hrs. into Fm^{254} which decays by spontaneous fission or by the emission of 7.2 Mev alpha particles. E^{254m} also decays by orbital electron capture to Cf^{254} in 0.1 percent of its disintegrations. E^{254} decays by the emission of 6.44 Mev alpha particles with a half-life of 272 days.[101, 102] This is the longest lived form of einsteinium.

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[99] B. G. Harvey, S. G. Thompson, A. Ghiorso, and G. R. Choppin, Phys. Rev. 93, 1129 (1954).

[100] P. R. Fields et al, Phys. Rev. 94, 209 (1954).

[101] B. G. Harvey, S. G. Thompson, G. R. Choppin, and A. Ghiorso, Phys. Rev. 99, 337 (1955).

[102] B. G. Harvey, S. G. Thompson, G. R. Choppin, and A. Ghiorso, unpublished results, 1955-1956.

Evidence has been found for the isotopes E^{249}, E^{251}, and E^{252} produced in helium bombardments of Bk^{249}.[102]

Data on the isotopes of einsteinium are summarized in Table 26.

The decay scheme of E^{253} is shown in Figure 29.

Figure 29. Decay scheme of E^{253}.

Table 26. Isotopes of Einsteinium

Isotope and Half-life	Type of Decay	Energy (Mev)	Method of Production
E^{246} minutes(1)	E.C.		$U^{238} + {}_7N^{14}$
E^{247}(?) 7.3 min (1)	α	7.35(1)	$U^{238} + {}_7N^{14}$
E^{249} 2hours (2)	α	6.76(2)	$Bk^{249}(\alpha, 4n)$(2)
E^{251} 1.5 days(2)	α E.C.>99%	6.48(2)	$Bk^{249}(\alpha, 2n)$(2)
E^{252} >20 days	α	6.64(2)	$Bk^{249}(\alpha, n)$(2)
E^{253}(3) 19.3 days(4) 20 days (5, 7)	α	6.61(4) 6.63(5) 6.633(91%)6.592(8%) 6.543(1%)6.491(0.3%) (6)	U^{238}(MNC)*(3) Pu^{239}(MNC)(7, 8) β^- daughter Cf^{253}(3) E.C. daughter Fm^{253}(2)
E^{254m} 36 hours (5) 37 hours (4)	β^- E.C.(0.1%) (10, 12) I.T. not ob.	1.1 (5)	$E^{253}(n, \gamma)$(9, 4)
E^{254} 272 days(2)	α	6.44(10)	$E^{253}(n, \gamma)$(10)
E^{255} 30 days (3, 5)	β^-		U^{238}(MNC)*(3)
E^{256} short (hours or less)	β^-		$E^{255}(n, \gamma)$

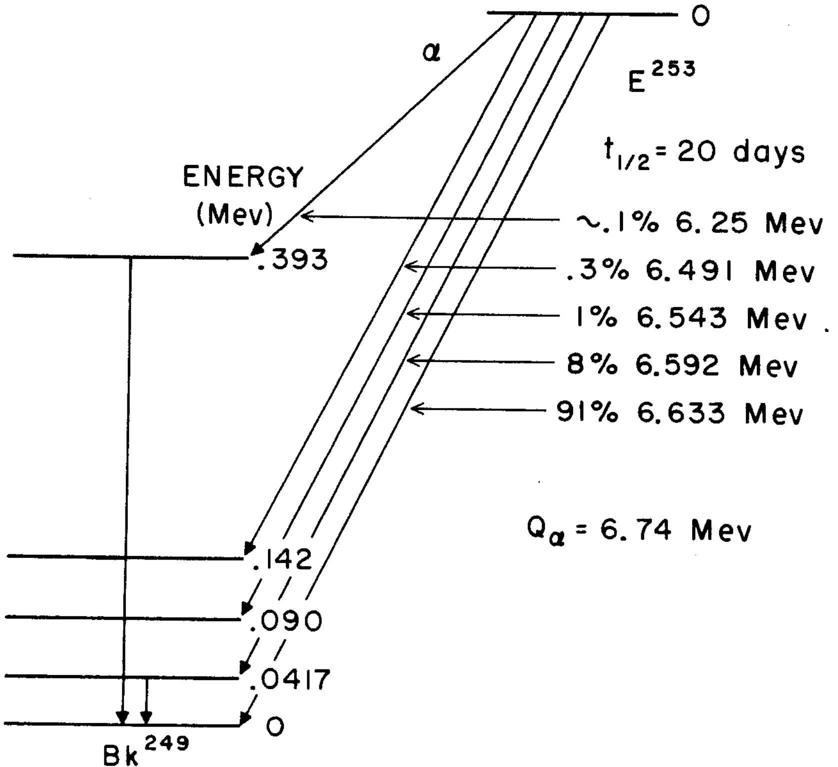
*MNC means multiple neutron capture.

[1] A. Ghiorso et al, Phys. Rev. 93, 257 (1954).

[2] B. G. Harvey, S. G. Thompson, G. R. Choppin, A. Ghiorso and A. Chetham Strode, unpublished results, December 1955.

[3] A. Ghiorso et al, Phys. Rev. 99, 1048 (1955).

[4] P. R. Fields et al, Phys. Rev. 94, 209 (1954).



0
α
E^{253}
$t_{1/2}$ = 20 days
ENERGY
(Mev)
~.1% 6.25 Mev
.3% 6.491 Mev
1% 6.543 Mev
8% 6.592 Mev
91% 6.633 Mev
Q_α = 6.74 Mev
.393
.142
.090
.0417
0
Bk^{249}
MU-10874

Figure 29

[5] G. R. Choppin *et al*, Phys. Rev. **94**, 1080 (1954).

[6] J. Hummel, University of California Radiation Laboratory, unpublished information.

[7] M. H. Studier, *et al*, Phys. Rev. **93**, 1428 (1954).

[8] S. G. Thompson, *et al*, Phys. Rev. **93**, 908 (1954).

[9] B. G. Harvey, *et al*, Phys. Rev. **93**, 1129 (1954).

[10] B. G. Harvey, *et al*, Phys. Rev. **99**, 337 (1955).

[11] G. R. Choppin *et al*, Phys. Rev. **98**, 1519 (1955).

[12] W. C. Bentley, et al, Paper P/809, "Peaceful Uses of Atomic Energy - Proceedings of the Geneva Conference", August, 1955, United Nations

55. Chemical properties of einsteinium. Einsteinium is the tenth member of the actinide 5f transition series. To date its chemical properties have been studied only on the tracer scale in aqueous solution. Its behavior in every respect is that expected of a tripositive actinide ion. The chemistry of einsteinium has been described by Thompson, Harvey, Choppin, and Seaborg.[103] Einsteinium will coprecipitate with rare-earth hydroxides or fluorides. It will extract into the solvent, tributyl phosphate, from an aqueous dilute nitric acid solution highly salted with neutral nitrates.[104] It will form a chelate complex with the beta-diketone thenoyltrifluoroacetone, which is readily extracted into benzene from an aqeuous solution of pH 3.4.[105]

The major emphasis in einsteinium chemistry has been concerned with ion exchange elution separations of einsteinium from the rare-earths and from the other actinide elements. Einsteinium is readily absorbed on Dowex-50 cation exchange resin. When 13 molar hydrochloric acid is used as an eluting agent einsteinium is readily desorbed ahead of the rare-earths indicating a stronger tendency to form chloride complexes. Somewhat sharper results are achieved when 20 percent ethyl alcohol saturated with hydrochloric acid is used as the eluting agent and colloidal Dowex-50 resin, 12 percent cross-linked is used.[103,106] Figure 30 shows an elution curve using this reagent. The rare earths elute well after curium and are hence very completely separated from einsteinium. The einsteinium elution peak is seen to be cleanly separated from berkelium and lower actinide elements but not from elements 98 or 100.

Figure 30. (Top) Elution of trace amounts of actinide elements from a 5 cm length by 3 mm diameter column of Dowex-50 12 percent cross-linked colloidal cation exchange resin. Eluting agent - 20 percent alcohol - 12.5 molar hydrochloric acid.
(Bottom) Elution of trace amounts of actinide elements from 5 cm length by 3 mm diameter column of Dowex-1 anion exchange resin (8 percent cross-linked) with 13 molar hydrochloric acid. Figure produced from Reference 103.

---

[103] S. G. Thompson, B. G. Harvey, G. R. Choppin, and G. T. Seaborg, J. Am. Chem. Soc. 76, 6229 (1954).

[104] M. H. Studier et al, Phys. Rev. 93, 1428 (1954).

[105] L. B. Magnussen and M. L. Anderson, J. Am. Chem. Soc. 76, 6207 (1954).

[106] K. Street, Jr., unpublished work.

After the rare earths are removed by the hydrochloric acid elution separation the einsteinium is separated from the other actinide elements by adsorbing the mixture of actinide elements on a column of cation exchange resin and eluting with a buffered solution of a suitable organic acid. Some acids which have been studied, in the order of their effectiveness in separating these elements, are citric acid, lactic acid, and α-hydroxyisobutyrate. A sample elution curve with α-hydroxyisobutyrate, the best of these organic acid complexing agents, is shown in Figure 31.[107]

In concentrated solutions of hydrochloric acid einsteinium forms anionic chloride complexes which can be adsorbed on an anion exchange resin such as Dowex-A1. If additional concentrated hydrochloric acid is passed through the anion exchange column the einsteinium is eluted rather quickly from the column, but with a delay sufficient to effect a separation from the actinide elements below californium which elute faster. Figure 30 shows the extent of the separation which can be achieved. In this separation, the lanthanide elements do not adsorb and appear in the free column volume of elutrient. Instead of hydrochloric acid it is also possible to use very concentrated solutions of lithium chloride. Negatively charged complexes of einsteinium are also found in concentrated solutions of ammonium thiocyanate.[108]

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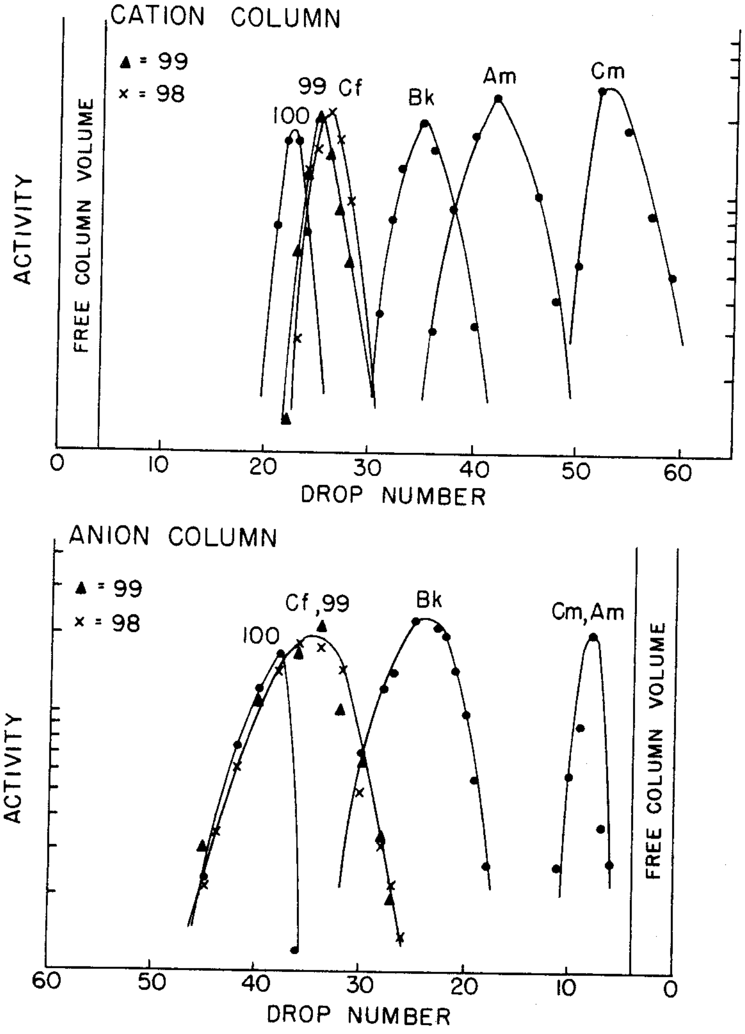
[107] G. R. Choppin, B. G. Harvey, and S. G. Thompson, J. Inorg. and Nucl. Chem. 2, (1956) ; G. R. Choppin and R. Silva, University of California Radiation Laboratory Report UCRL-3265 (1956).

[108] J. P. Surls, Jr., unpublished results quoted by S. G. Thompson, et al in Reference 103; see also J. P. Surls, Jr., University of California Radiation Laboratory Report UCRL-3209 (1955).

Early in 1956 the amounts of einsteinium available for study were in the range of 10^7 alpha disintegrations per minute of 20 day E^{253}. Due to the existence of the long-lived E^{254} isomer weighable amounts of einsteinium will be available eventually for more detailed chemical and physical studies.

Figure 31. Elution of actinide elements from a 5 cm x 2 mm column of 12 percent cross-linked Dowex-50 cation exchange resin by 0.4 molar ammonium alpha-hydroxyisobutyrate. The column was operated at 87° C. Figure reproduced from Reference 107.



MU-7817

Figure 30

VIII. FERMIUM (ELEMENT 100)

56. Discovery of fermium - summary of known isotopes. The first isotope of element 100 to be identified was 100^{255}, a 16-hour activity decaying by the emission of 7.1 Mev alpha particles. It was found in the heavy element fractions from the "Mike" thermonuclear explosion of November 1952 in the same set of experiments which resulted in the discovery of einsteinium, element 99. These experiments are summarized briefly in Section 54. It was also recorded in Section 54 that the name fermium (symbol Fm) was given to element 100 in honor of Enrico Fermi.

A second isotope of fermium, Fm^{254}, is produced when californium samples rich in Cf^{252},[109] or einsteinium samples rich in E^{253},[110,111] are subjected to intense neutron irradiation. The reaction sequence is:

$$\begin{tikzcd} Cf^{252}(n,\gamma) & Cf^{253} \arrow[d, "\beta^-"', "20\text{ days}"] & \\ & E^{253}(n,\gamma) & E^{254m} \arrow[d, "\beta^-"', "36\text{ hours}"] \\ & & Fm^{254} \end{tikzcd} \qquad (52.1)$$

Fm^{254} decays by the emission of 7.2 Mev alpha particles with a half-life of 3.2 hours. It also decays by spontaneous fission with a partial half-life of 220 days. The genetic relationship of the 36-hour E^{254m} and Fm^{254} was firmly established by observing the growth of Fm^{254} radiations into a purified einsteinium fraction.[110,111]

The isotope Fm^{256} was prepared[112] by irradiating an einsteinium sample containing a small amount of 30-day E^{255} mixed with E^{253}. Spontaneous fission events assigned to Fm^{256} were found in the chemically separated fermium fraction from this bombardment. The observed half-life was 3 to 4 hours.

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[109] B. G. Harvey, S. G. Thompson, A. Ghiorso, and G. R. Choppin, Phys. Rev. 93, 1129 (1954).

[110] P. R. Fields, et al, Phys. Rev. 94, 209 (1954).

[111] G. R. Choppin, S. G. Thompson, A. Ghiorso, and B. G. Harvey, Phys. Rev. 94, 1080 (1954).

[112] G. R. Choppin, B. G. Harvey, S. G. Thompson, and A. Ghiorso, Phys. Rev. 98, 1519 (1955).

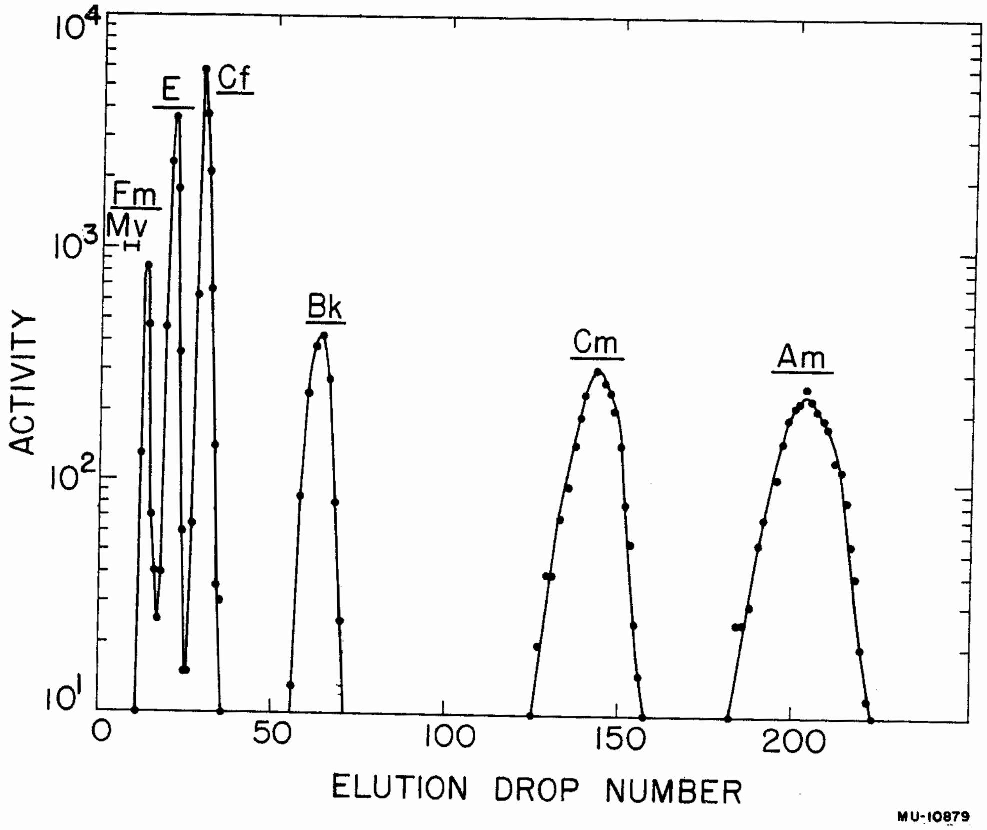
10^4
10^3
10^2
10^1
ACTIVITY
Fm
Mv
E
Cf
Bk
Cm
Am
0
50
100
150
200
ELUTION DROP NUMBER
MU-10879

Figure 31

A Swedish research team[113] bombarded uranium targets with hextuplicately charged O^{16} ions accelerated in a cyclotron to greater than 180 Mev energy. After chemical purification an examination of the fraction corresponding to the element 100 fraction was carried out and some 7.7 Mev alpha activity decaying with a half-life of about 1/2 hour was found. The tentative mass assignment of this activity was 100^{250}.

Fermium isotopes have been prepared by bombarding targets of californium with helium ions in the Berkeley 60-inch cyclotron.[114] The californium targets contained a high percentage of the heavy isotopes Cf^{249}, Cf^{250}, Cf^{251}, and Cf^{252}. In this way Fm^{254}, Fm^{253} (not clearly identified), Fm^{252}, and Fm^{250} were observed.

The data on the fermium isotopes are summarized in Table 27. The spontaneous fission half-lives for the even-even isotopes of fermium are of the same order of magnitude as the alpha decay half-lives. This matter will be discussed in a later section of this report.

The decay scheme of Fm^{254} is shown in Figure 32.

Figure 32. The decay scheme of Fm^{254}.

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[113] H. Atterling, W. Forsling, L. W. Holm, L. Melander, and B. Aström Phys. Rev. 95, 585 (1954).

[114] B. G. Harvey and co-workers, University of California Radiation Laboratory, unpublished results, January 1956.

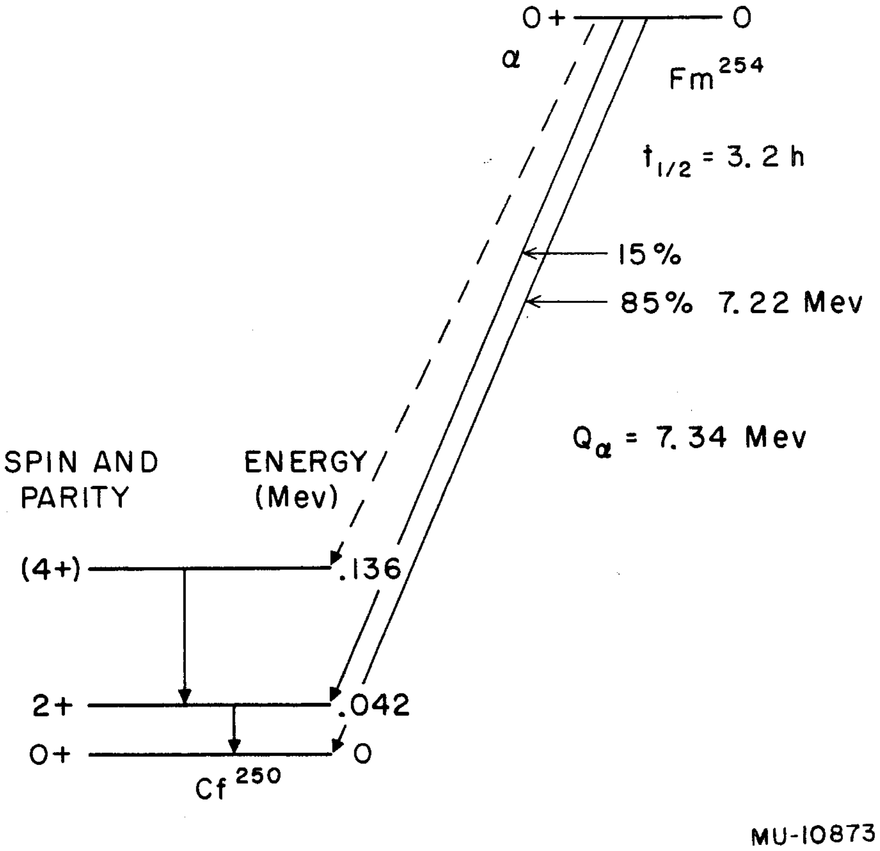
0+
0
α
Fm^{254}
$t_{1/2}$ = 3.2 h
15%
85% 7.22 Mev
Q_α = 7.34 Mev
SPIN AND PARITY
ENERGY (Mev)
(4+)
.136
2+
.042
0+
0
Cf^{250}
MU-10873

Figure 32

Table 27. Isotopes of Fermium

Isotope and Half-life	Type of Decay	Energy(Mev)	Production
$Fm^{250(?)}$ 30 min. (Ref. 1)	α	7.7 (Ref. 1)	$U^{238}(O^{16}, 4n)$ (Ref. 1)
Fm^{250} ~1/2 hour (Ref. 2)	α	7.43 (Ref. 2)	$Cf^{249-252}(\alpha, xn)$(Ref. 2)
Fm^{252} 30 hours	α	7.1 (Ref. 2)	Pu^{239} (multiple neutron capture)(Ref. 3) $Cf^{249-252}(\alpha, xn)$(Ref. 2)
Fm^{253} days(?)	E. C.		$Cf^{249-252}(\alpha, xn)$(Ref. 2)
Fm^{254} 3.2 hours(Ref. 4) 3.3 hours(Ref. 5) 220 days spon. fiss. (Ref. 4, 5)	α Spon. Fiss.	7.22	daughter E^{254m} Pu^{239}(multiple neutron capture)
Fm^{255}(Ref. 6) 16 hours (Ref. 6) 21.5 hours (Ref. 3)	α	7.1 (Ref. 6)	Pu^{239}(multiple neutron capture) U^{238}(multiple neutron capture) (Ref. 6)
Fm^{256}(Ref. 7) 3 hours (Ref. 3)	Spon. Fiss.		$E^{255}(n, \gamma)E^{256} \xrightarrow{\beta^-}$

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[1] H. Atterling, *et al*, Phys. Rev. **95**, 585 (1954).

[2] S. G. Thompson *et al*, unpublished results, University of California Radiation Laboratory, December 1955.

[3] B. G. Harvey, *et al.* unpublished results, University of California Radiation Laboratory, 1955.

[4] G. R. Choppin, *et al*, Phys. Rev. **94**, 1080 (1954).

[5] P. R. Fields, *et al.*, Phys. Rev. **93**, 1428 (1954).

[6] Phys. Rev. **99**, 1048 (1955).

[7] G. R. Choppin, *et al*, Phys. Rev. **98**, 1519 (1955).

57. Chemical properties of fermium. Fermium is the eleventh member of the actinide transition series. The chemical properties have been studied only on a tracer scale. The conclusions from these studies are that fermium exists as the tripositive ion in aqueous solution and that its chemical properties are entirely similar to the tripositive ions of the other actinide elements. The ion exchange elution technique has been used to separate fermium cleanly from rare-earth and actinide element contaminants. These properties of fermium are apparent from the discussion of Section 55 and the curves in Figures 30 and 31 in Section 55.

IX. MENDELEVIUM (ELEMENT 101)

58. Discovery of mendelevium. An isotope of element 101 believed to be 101^{256} was produced and identified by Ghiorso, Harvey, Choppin, Thompson, and Seaborg early in 1955 by bombarding extremely minute targets of E^{253} with 41 Mev helium ions in the Berkeley 60-inch cyclotron.[115] Chemical separations were carried out after bombardment using the ion-exchange elution techniques employed previously in the discovery of elements 97 through 100. In the eka-thulium elution position, i.e., the element 101 elution position, a few spontaneously-fissionable atoms were found. The half-life for the decay of these atoms numbering a combined total of only 17 from the summation of many experiments, was approximately 3.5 hours. The interpretation of the results was that 101^{256} was produced by the reaction:

$$E^{253}(\alpha, n)101^{256}. \qquad (54.1)$$

The isotope 101^{256} decays by electron capture with a half-life of the order of a half-hour to Fm^{256},

$$101^{256} \xrightarrow[\backsim 1/2\ \text{hr}]{\text{E.C.}} Fm^{256}$$

The Fm^{256} then decays by spontaneous fission with a half-life of about 3.5 hours. The radiations of element 101 itself were not observed. These results were later confirmed with substantially greater amounts of E^{253} target material,[116] leading to the chemical identification of some hundreds of atoms of the new element.

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[115] A. Ghiorso, B. G. Harvey, G. R. Choppin, S. G. Thompson, and G. T. Seaborg, Phys. Rev. 98, 1518 (1955).

[116] B. G. Harvey, S. G. Thompson, G. R. Choppin, and A. Ghiorso, unpublished work, January 1956.

Special bombardment techniques had to be developed to carry out these experiments effectively, safely, and quickly.

The name mendelevium (symbol Mv) was suggested for element 101 in recognition of the pioneering role of the great Russian chemist, Dimitri Mendeleev, in the use of the periodic system of the elements.

It may be expected that several mendelevium isotopes covering the mass number range 251 -261 will be found with half-lives of the order of a few seconds to an hour.[117]

The production of mendelevium by intense neutron irradiation of lighter elements is not promising because it is necessary to build up the mass number of the fermium fraction to 259 before beta decay to an isotope of mendelevium occurs. The sequence would be:

$$\ldots\ldots\ldots\ldots\ldots Fm^{254}(n,\gamma)Fm^{255}(n,\gamma)Fm^{256}(n,\gamma)Fm^{257}(n,\gamma)Fm^{258}(n,\gamma)$$

$$\begin{array}{l} Fm^{259} \\ \downarrow \\ Mv^{259} \end{array}$$

The difficulty is that Fm^{256} has a half-life for spontaneous fission of only three hours and Fm^{258} probably has a half-life for spontaneous fission of much less than this, so the reaction path to mendelevium is effectively blocked.

59. Chemical properties of mendelevium. Mendelevium is the twelfth member of the actinide transition series. As such it is expected to show only the tripositive oxidation state in solution and is expected to resemble quite closely the chemical properties of the tripositive actinide elements. The ion exchange elution behavior will be of chief importance in radiochemical purification. This behavior may be summarized as follows:

Mendelevium will adsorb readily on cation exchange resin columns. If buffered citrate, lactate, alpha-hydroxyisobutyrate, or similar agents are used as an eluting agent, mendelevium will elute from the column just ahead of fermium. If saturated hydrochloric acid or 20 percent ethyl alcohol saturated with hydrochloric acid is used as the eluting agent

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[117] R. A. Glass, S. G. Thompson, and G. T. Seaborg, J. Inorg. and Nucl. Chem. 1, 3 (1955).

mendelevium will elute just ahead of fermium and will be more completely separated from the rare earths than any of the tripositive actinide elements of lower atomic number. Mendelevium will adsorb on anion exchange resins from 13 molar hydrochloric acid. If 13 molar hydrochloric acid is used as an eluting agent mendelevium will elute with fermium or slightly after.

C. SYSTEMATICS OF NUCLEAR DATA IN THE TRANSURANIUM ELEMENT REGION

I. NUCLEAR THERMODYNAMICS

60. Closed decay-energy cycles. The purpose of this section is to summarize in graphical and tabular form the extensive data on disintegration energies for the transuranium element region. For a more complete treatment of this subject and for references to the original literature pertaining to this subject or to basic data, the reader is referred to the extensive articles of Glass, Thompson and Seaborg,[1] Newton,[2] Perlman, Ghiorso, and Seaborg,[3] and Huizenga.[4] The data presented in the following figures and tables represents a revision of the data of Glass, et al[1] using newer data available as of January 1956. For these revisions the authors are indebted to Mr. Bruce M. Foreman, Jr.

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[1] R. A. Glass, S. G. Thompson, and G. T. Seaborg, J. Inorg. Nucl. Chem. 1, 3, (1955).

[2] J. O. Newton, "Progress in Nuclear Physics" 4, 234-286 (1955).

[3] I. Perlman, A. Ghiorso, and G. T. Seaborg, Phys. Rev. 77, 26 (1950).

[4] J. R. Huizenga, Physica 21, 410 (1955).

In the heavy element region the existence of alpha decay instability and beta decay instability in the same nucleus has made it possible to construct closed decay-energy cycles. Such cycles are extremely useful in checking the internal consistency of the decay data and in predicting unknown properties. Consider for example, the cycles shown in Figure 33 involving a few isotopes of the 4n+1 family of isotopes. In the cycle containing Np^{237}-Am^{241}-Pu^{241} and U^{237} experimental data are available on all four sides of the data cycle and these are mutually consistent, i.e., the summation of decay energies around the complete cycle is zero. In those cases where experimental data or reliable estimates are available for three branches of the cycle, the fourth can then be calculated by difference. A systematic extension of the closed decay-energy cycle method to cover the entire transuranium element region is given in Figures 34-37. Since alpha decay decreases the mass number of a decaying nucleus by four and beta processes leave the mass number unchanged all isotopes in a given figure differ in mass by multiples of four. Hence four figures are required to present the data for the 4n, 4n+1, 4n+2, and 4n+3 mass types.

Figure 33. Decay cycles for part of 4n+1 family. Code ← α decay, ↑ β^- decay, ↓ electron capture decay. Numerals indicate total decay energies in Mev; those with superscript c are calculated by closing the cycles; those with superscript e are estimated by methods of sections 61, those unmarked are measured values.

Figure 34. Closed decay-energy cycles for the 4n family. Code: no superscript, measured energy; c, calculated energy; cn, calculated with neutron binding energies; e, estimated; ( ), uncertain by more than 0.1 Mev.

Figure 35. Closed decay energy cycles for the 4n+1 family. For code see Figure 34.

Figure 36. Closed decay energy cycles for the 4n+2 family. For code see Figure 34.

Figure 37. Closed decay energy cycles for the 4n+3 family. For code see Figure 34.

In Figures 34-37 approximately one-fourth of the energy values listed represent directly determined values. Approximately one-half of the values were estimated from the graphs showing systematic trends in alpha and beta disintegration energies which will be discussed in Sections 61 and 62. A final group of energies was calculated by closing decay cycles after the experimental and estimated values were entered. Since any given disintegration energy is common to two decay cycles opportunities arise for cross-checking the experimental or estimated values.

In the construction of Figures 34-37 any inconsistencies which arise (usually in the vertical branches) were settled after due consideration of possible sources of error and suitable adjustments were made to give the best possible self-consistent set of decay energies. These energy cycles refer only to the ground-state transitions and provide no information on decay to excited levels in the daughter nucleus. The only exception to this is in the case of the isomer pairs of Pa^{234}, Am^{242}, and Np^{240} where data referring to the upper and lower state are included.

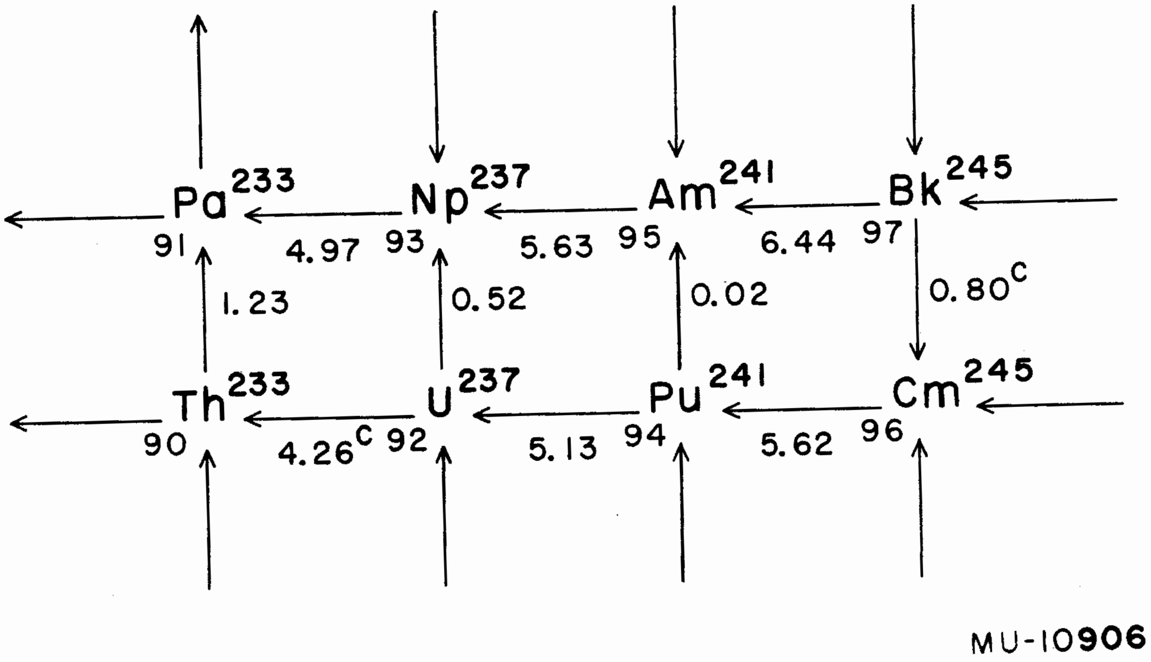
Pa233
Np237
Am241
Bk245
91
4.97
93
5.63
95
6.44
97
1.23
0.52
0.02
0.80c
Th233
U237
Pu241
Cm245
90
4.26c
92
5.13
94
5.62
96
MU-10906

Figure 33

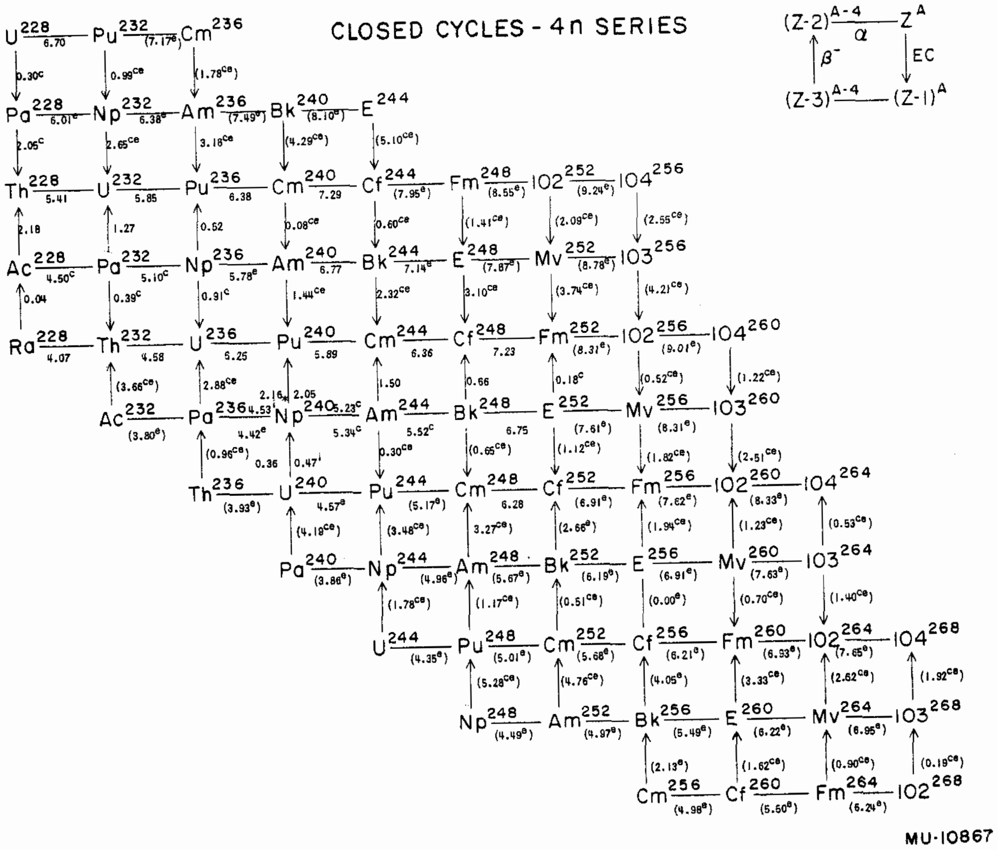
CLOSED CYCLES - 4n SERIES
(Z-2)A-4 α Z A
β- EC
(Z-3)A-4 (Z-1)A
U228 6.70 Pu232 (7.17e) Cm236
0.30c 0.99ce (1.78ce)
Pa228 6.01e Np232 6.38e Am236 (7.49e) Bk240 (8.10e) E244
2.05c 2.65ce 3.18ce (4.29ce) (5.10ce)
Th228 5.41 U232 5.85 Pu236 6.38 Cm240 7.29 Cf244 (7.95e) Fm248 (8.55e) 102 252 (9.24e) 104 256
2.18 1.27 0.52 0.08ce 0.60ce (1.41ce) (2.09ce) (2.55ce)
Ac228 4.50c Pa232 5.10c Np236 5.78e Am240 6.77 Bk244 7.14e E248 (7.87e) Mv252 (8.78e) 103 256
0.04 0.39c 0.91c 1.44ce 2.32ce 3.10ce (3.74ce) (4.21ce)
Ra228 4.07 Th232 4.58 U236 5.25 Pu240 5.89 Cm244 6.36 Cf248 7.23 Fm252 (8.31e) 102 256 (9.01e) 104 260
(3.66ce) 2.88ce 2.16 2.05 1.50 0.66 0.18c (0.52ce) (1.22ce)
Ac232 (3.80e) Pa236 4.53 4.42e Np240 5.23c 5.34c Am244 5.52c Bk248 6.75 E252 (7.61e) Mv256 (8.31e) 103 260
(0.96ce) 0.36 0.47i 0.30ce (0.65ce) (1.12ce) (1.82ce) (2.51ce)
Th236 (3.93e) U240 4.57e Pu244 (5.17e) Cm248 6.28 Cf252 (6.91e) Fm256 (7.62e) 102 260 (8.33e) 104 264
(4.19ce) (3.48ce) 3.27ce (2.66e) (1.94ce) (1.23ce) (0.53ce)
Pa240 (3.86e) Np244 (4.96e) Am248 (5.67e) Bk252 (6.19e) E256 (6.91e) Mv260 (7.63e) 103 264
(1.78ce) (1.17ce) (0.51ce) (0.00e) (0.70ce) (1.40ce)
U244 (4.35e) Pu248 (5.01e) Cm252 (5.68e) Cf256 (6.21e) Fm260 (6.93e) 102 264 (7.65e) 104 268
(5.28ce) (4.76ce) (4.05e) (3.33ce) (2.62ce) (1.92ce)
Np248 (4.49e) Am252 (4.97e) Bk256 (5.49e) E260 (6.22e) Mv264 (6.95e) 103 268
(2.13e) (1.62ce) (0.90ce) (0.19ce)
Cm256 (4.98e) Cf260 (5.60e) Fm264 (6.24e) 102 268
MU-10867

Figure 34

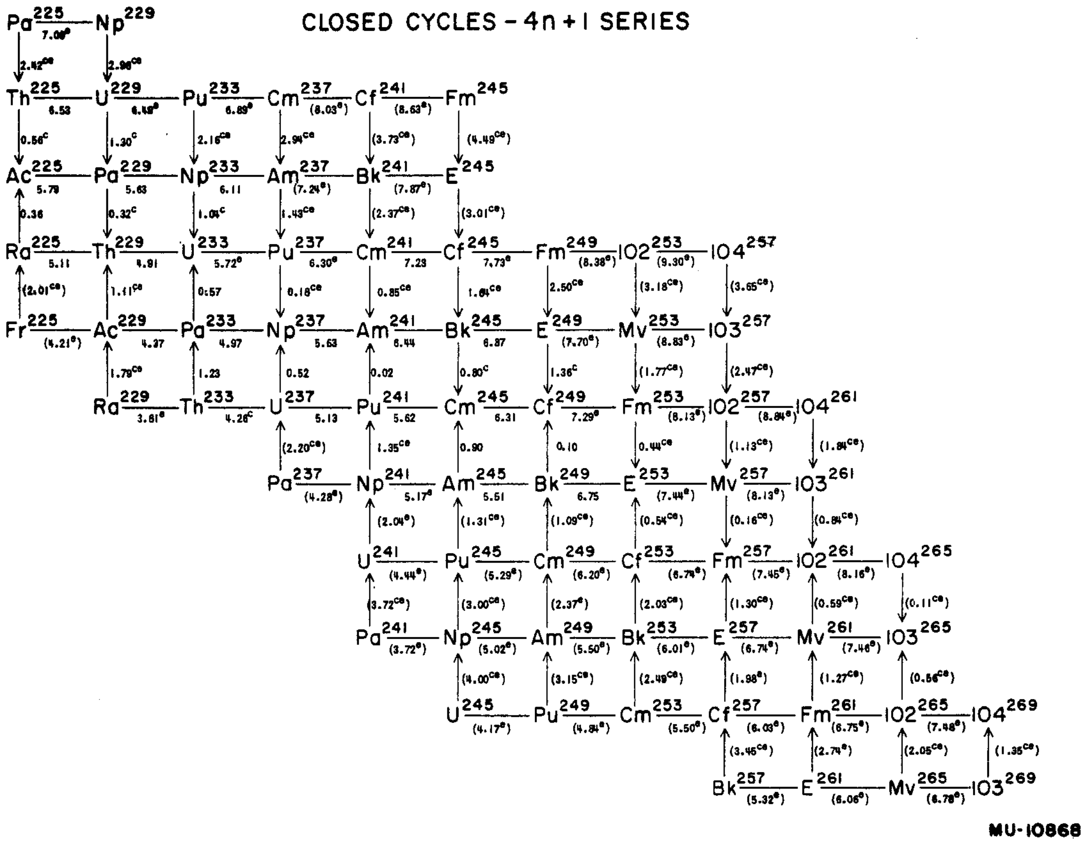
CLOSED CYCLES - 4n + 1 SERIES
Pa^{225} 7.08^{e} Np^{229}
2.42^{ce} 2.96^{ce}
Th^{225} 6.53 U^{229} 6.49^{e} Pu^{233} 6.89^{e} Cm^{237} (8.03^{e}) Cf^{241} (8.63^{e}) Fm^{245}
0.56^{c} 1.30^{c} 2.16^{ce} 2.94^{ce} (3.73^{ce}) (4.49^{ce})
Ac^{225} 5.79 Pa^{229} 5.63 Np^{233} 6.11 Am^{237} (7.24^{e}) Bk^{241} (7.87^{e}) E^{245}
0.36 0.32^{c} 1.04^{c} 1.43^{ce} (2.37^{ce}) (3.01^{ce})
Ra^{225} 5.11 Th^{229} 4.91 U^{233} 5.72^{e} Pu^{237} 6.30^{e} Cm^{241} 7.23 Cf^{245} 7.73^{e} Fm^{249} (8.38^{e}) 102^{253} (9.30^{e}) 104^{257}
(2.01^{ce}) 1.11^{ce} 0.57 0.18^{ce} 0.85^{ce} 1.64^{ce} 2.50^{ce} (3.18^{ce}) (3.65^{ce})
Fr^{225} (4.21^{e}) Ac^{229} 4.37 Pa^{233} 4.97 Np^{237} 5.63 Am^{241} 6.44 Bk^{245} 6.87 E^{249} (7.70^{e}) Mv^{253} (8.83^{e}) 103^{257}
1.79^{ce} 1.23 0.52 0.02 0.80^{c} 1.36^{c} (1.77^{ce}) (2.47^{ce})
Ra^{229} 3.61^{e} Th^{233} 4.26^{c} U^{237} 5.13 Pu^{241} 5.62 Cm^{245} 6.31 Cf^{249} 7.29^{e} Fm^{253} (8.13^{e}) 102^{257} (8.84^{e}) 104^{261}
(2.20^{ce}) 1.35^{ce} 0.90 0.10 0.44^{ce} (1.13^{ce}) (1.84^{ce})
Pa^{237} (4.28^{e}) Np^{241} 5.17^{e} Am^{245} 5.51 Bk^{249} 6.75 E^{253} (7.44^{e}) Mv^{257} (8.13^{e}) 103^{261}
(2.04^{e}) (1.31^{ce}) (1.09^{ce}) (0.54^{ce}) (0.16^{ce}) (0.84^{ce})
U^{241} (4.44^{e}) Pu^{245} (5.29^{e}) Cm^{249} (6.20^{e}) Cf^{253} (6.74^{e}) Fm^{257} (7.45^{e}) 102^{261} (8.16^{e}) 104^{265}
(3.72^{ce}) (3.00^{ce}) (2.37^{e}) (2.03^{ce}) (1.30^{ce}) (0.59^{ce}) (0.11^{ce})
Pa^{241} (3.72^{e}) Np^{245} (5.02^{e}) Am^{249} (5.50^{e}) Bk^{253} (6.01^{e}) E^{257} (6.74^{e}) Mv^{261} (7.46^{e}) 103^{265}
(4.00^{ce}) (3.15^{ce}) (2.49^{ce}) (1.98^{e}) (1.27^{ce}) (0.56^{ce})
U^{245} (4.17^{e}) Pu^{249} (4.84^{e}) Cm^{253} (5.50^{e}) Cf^{257} (6.03^{e}) Fm^{261} (6.75^{e}) 102^{265} (7.48^{e}) 104^{269}
(3.45^{ce}) (2.74^{e}) (2.05^{ce}) (1.35^{ce})
Bk^{257} (5.32^{e}) E^{261} (6.06^{e}) Mv^{265} (6.78^{e}) 103^{269}
MU-10868

Figure 35

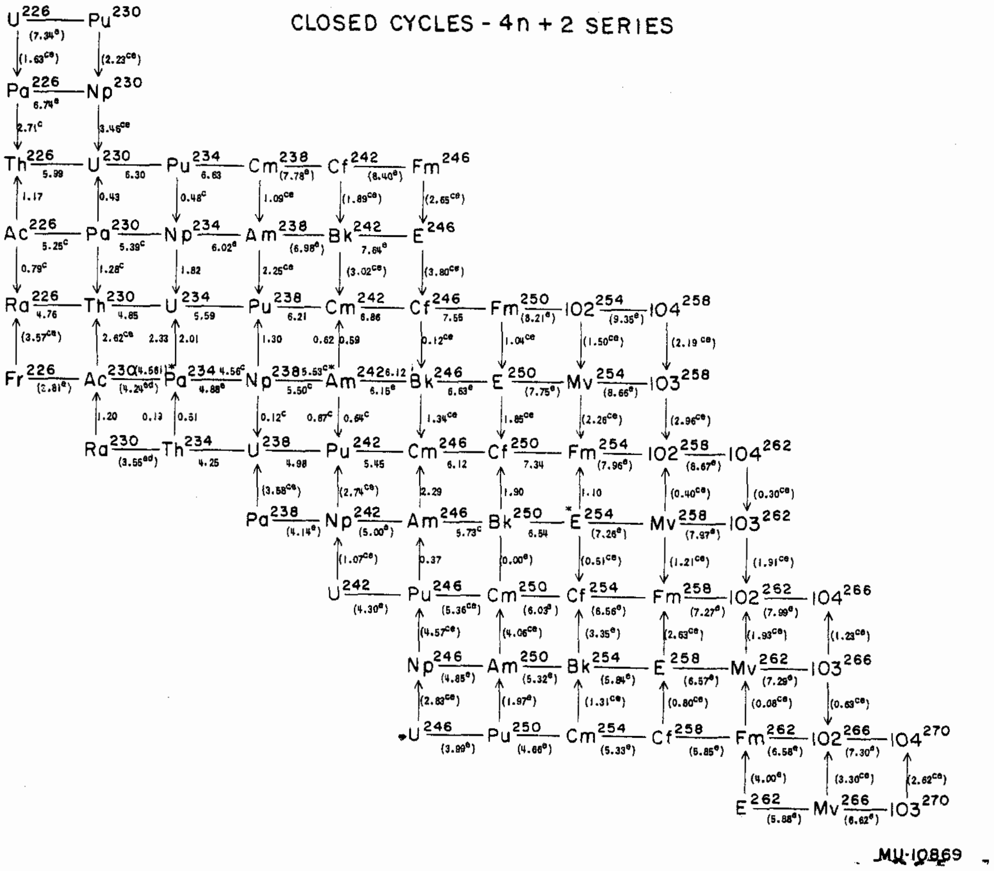
CLOSED CYCLES - 4n + 2 SERIES
U226 Pu230
Pa226 Np230
Th226 U230 Pu234 Cm238 Cf242 Fm246
Ac226 Pa230 Np234 Am238 Bk242 E246
Ra226 Th230 U234 Pu238 Cm242 Cf246 Fm250 102 254 104 258
Fr226 Ac230 Pa234 Np238 Am242 Bk246 E250 Mv254 103 258
Ra230 Th234 U238 Pu242 Cm246 Cf250 Fm254 102 258 104 262
Pa238 Np242 Am246 Bk250 E254 Mv258 103 262
U242 Pu246 Cm250 Cf254 Fm258 102 262 104 266
Np246 Am250 Bk254 E258 Mv262 103 266
U246 Pu250 Cm254 Cf258 Fm262 102 266 104 270
E262 Mv266 103 270
MU-10869

Figure 36

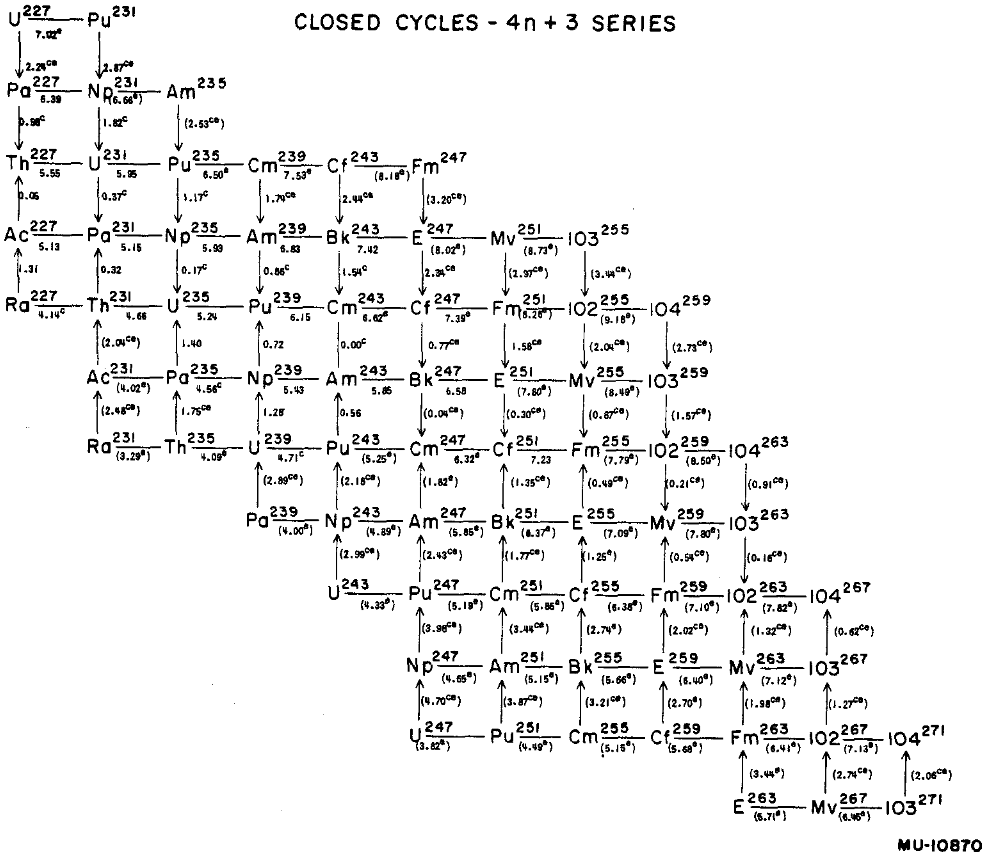
CLOSED CYCLES - 4n + 3 SERIES
U^{227} 7.02^{e} Pu^{231}
2.24^{ce} 2.87^{ce}
Pa^{227} 6.39 Np^{231} (6.66^{e}) Am^{235}
0.98^{c} 1.82^{c} (2.53^{ce})
Th^{227} 5.55 U^{231} 5.95 Pu^{235} 6.50^{e} Cm^{239} 7.53^{e} Cf^{243} (8.18^{e}) Fm^{247}
0.06 0.37^{c} 1.17^{c} 1.74^{ce} 2.44^{ce} (3.20^{ce})
Ac^{227} 5.13 Pa^{231} 5.15 Np^{235} 5.93 Am^{239} 6.83 Bk^{243} 7.42 E^{247} (8.02^{e}) Mv^{251} (8.73^{e}) 103^{255}
1.31 0.32 0.17^{c} 0.86^{c} 1.54^{c} 2.34^{ce} (2.97^{ce}) (3.44^{ce})
Ra^{227} 4.14^{c} Th^{231} 4.66 U^{235} 5.24 Pu^{239} 6.15 Cm^{243} 6.62^{e} Cf^{247} 7.39^{e} Fm^{251} (8.26^{e}) 102^{255} (9.18^{e}) 104^{259}
(2.04^{ce}) 1.40 0.72 0.00^{c} 0.77^{ce} 1.58^{ce} (2.04^{ce}) (2.73^{ce})
Ac^{231} (4.02^{e}) Pa^{235} 4.56^{c} Np^{239} 5.43 Am^{243} 5.86 Bk^{247} 6.58 E^{251} (7.80^{e}) Mv^{255} (8.49^{e}) 103^{259}
(2.48^{ce}) 1.75^{ce} 1.28 0.56 (0.04^{ce}) (0.30^{ce}) (0.87^{ce}) (1.57^{ce})
Ra^{231} (3.29^{e}) Th^{235} 4.09^{e} U^{239} 4.71^{c} Pu^{243} (5.25^{e}) Cm^{247} 6.32^{e} Cf^{251} 7.23 Fm^{255} (7.79^{e}) 102^{259} (8.50^{e}) 104^{263}
(2.89^{ce}) (2.18^{ce}) (1.82^{e}) (1.35^{ce}) (0.49^{ce}) (0.21^{ce}) (0.91^{ce})
Pa^{239} (4.00^{e}) Np^{243} (4.89^{e}) Am^{247} (5.85^{e}) Bk^{251} (6.37^{e}) E^{255} (7.09^{e}) Mv^{259} (7.80^{e}) 103^{263}
(2.99^{ce}) (2.43^{ce}) (1.77^{ce}) (1.25^{e}) (0.54^{ce}) (0.16^{ce})
U^{243} (4.33^{e}) Pu^{247} (5.19^{e}) Cm^{251} (5.86^{e}) Cf^{255} (6.38^{e}) Fm^{259} (7.10^{e}) 102^{263} (7.82^{e}) 104^{267}
(3.98^{ce}) (3.44^{ce}) (2.74^{e}) (2.02^{ce}) (1.32^{ce}) (0.62^{ce})
Np^{247} (4.65^{e}) Am^{251} (5.15^{e}) Bk^{255} (5.66^{e}) E^{259} (6.40^{e}) Mv^{263} (7.12^{e}) 103^{267}
(4.70^{ce}) (3.87^{ce}) (3.21^{ce}) (2.70^{e}) (1.98^{ce}) (1.27^{ce})
U^{247} (3.82^{e}) Pu^{251} (4.49^{e}) Cm^{255} (5.15^{e}) Cf^{259} (5.68^{e}) Fm^{263} (6.41^{e}) 102^{267} (7.13^{e}) 104^{271}
(3.44^{e}) (2.74^{ce}) (2.06^{ce})
E^{263} (5.71^{e}) Mv^{267} (6.46^{e}) 103^{271}
MU-10870

Figure 37

61. Alpha decay energy systematics. Figure 38 is a plot of alpha decay energies versus mass number where the points representing a given element have been connected. The decay energy refers to the ground-state transition and includes the nuclear recoil energy in addition to the energy of the alpha particle. Except for minor irregularities the alpha energies for isotopes of a given element generally decrease in a regular fashion with increasing mass number. Extensions of the experimental curves make it possible to predict unmeasured or unmeasurable disintegration energies between or beyond the measured ones.

In the curves for the elements californium, einsteinium, and fermium an irregularity occurs which reflects a discontinuity of the energy surface[*] in this mass region. The shell model of the nucleus proposed by Mayer[5] and Haxel, Jensen and Suess[6] predicts a large discontinuity in nuclear properties for isotopes in the region of 126 neutrons, since according to this theory 126 neutrons represents a completely filled major shell. The alpha disintegration energies for isotopes below the transuranium element region show a striking discontinuity of 3 to 4 Mev in the mass region which includes isotopes on both sides of the 126 neutron shell. The discontinuity which appears in Figure 38 is of a much smaller magnitude and has been ascribed to a "subshell" closure at 152 neutrons;[7] such a subshell is not predicted from a simple consideration of the shell model although it is consistent with it.

Figure 38. Alpha-decay energies for the isotopes of the transuranium elements as a function of mass number. Code: •, experimental value; □ calculated value; ▲, estimated value.

In the case of elements beyond element 100 for which no experimental points are available, lines have been placed in Figure 38 after due consideration of the spacings and slopes of the lines for elements 98, 99 and 100 including an allowance for a probable discontinuity at 152 neutrons. Values taken from

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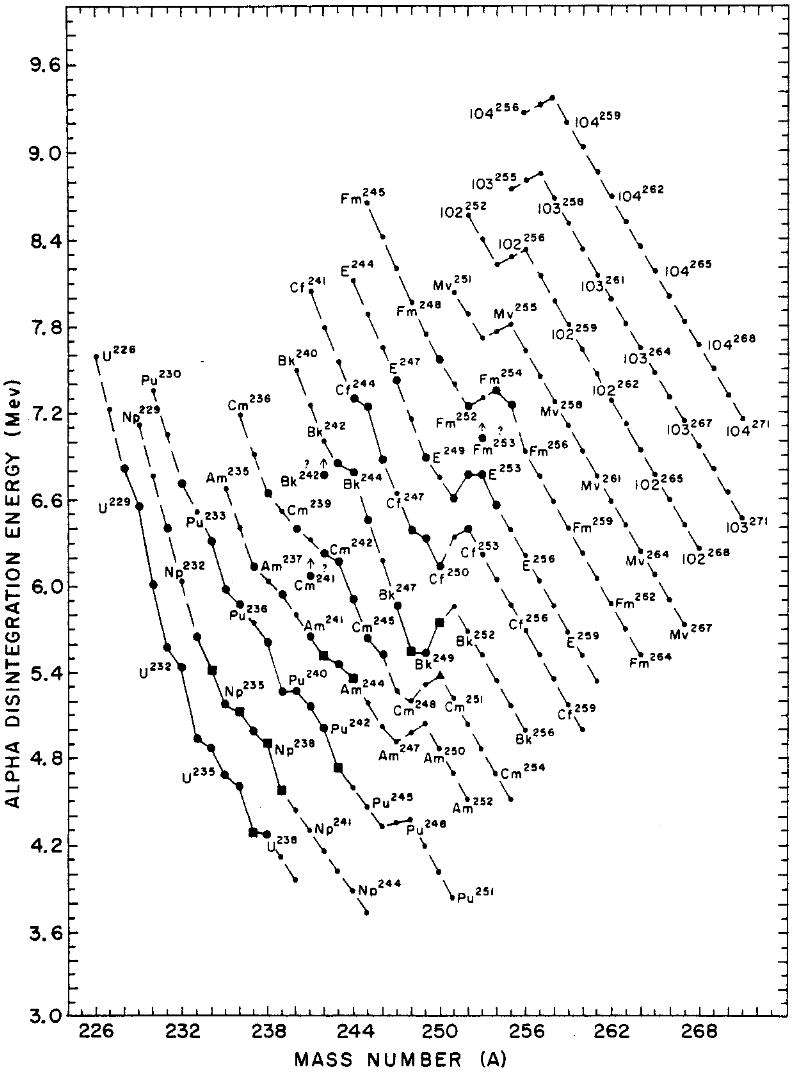
[5] M. G. Mayer, Phys. Rev. 75, 1969 (1949).

[6] O. Haxel, J. H. D. Jensen, and H. E. Suess, Z. Phys. 128, 295 (1950).

[7] A. Ghiorso, et al, Phys. Rev. 95, 293 (1954).

[*] "Energy-surface" refers to a surface defined by the energy contents or masses of the nuclides.



MU-10866

Figure 38

these lines are probably subject to more error than values taken from an extension of the curves for lower elements. Data taken from the curves of Figure 38 were used in the construction of the decay-energy cycles of Figures 34-37.

62. Beta-decay energy systematics. In Figure 39 the beta-decay energies for the transuranium element isotopes have been correlated with mass number. The upper part of the figure presents the data for even mass types while the lower part refers to the odd mass types.

Similar curves have been given by Way and Wood[8] and by Suess and Jensen[9]. The figures given here represent revisions of Figure 8, Reference 1, carried out by Mr. Bruce M. Foreman, Jr. The legend distinguishes those decay energies which are directly measured, those which are estimated, those calculated by closure of suitable decay cycles in Figures 34-37, and those calculated from decay cycles involving estimated alpha decay energies taken from Figure 38. Directly measured decay energies involve a knowledge of the decay scheme as well as of the maximum energies of the beta particle groups. In many instances unfortunately, the decay scheme is not known with certainty.

From Figures 39 or Figures 34-37, it is possible to determine which transuranium element isotopes are beta stable. This important information is summarized in Table 28.

Figure 39. Beta decay energies for the isotopes of the transuranium elements as a function of mass number. Code: ● , experimental energy; ○ , estimated energy; ■ energy calculated from closed decay-energy cycles; ▲ calculated from closed cycles which included estimated values. Upper part of curve refers to even mass types. Lower part refers to odd mass types.

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[8] K. Way and M. Wood, Phys. Rev. 94, 119 (1954).

[9] H. E. Suess and J. H. D. Jensen, Arkiv. Fysik 3, 577 (1951).

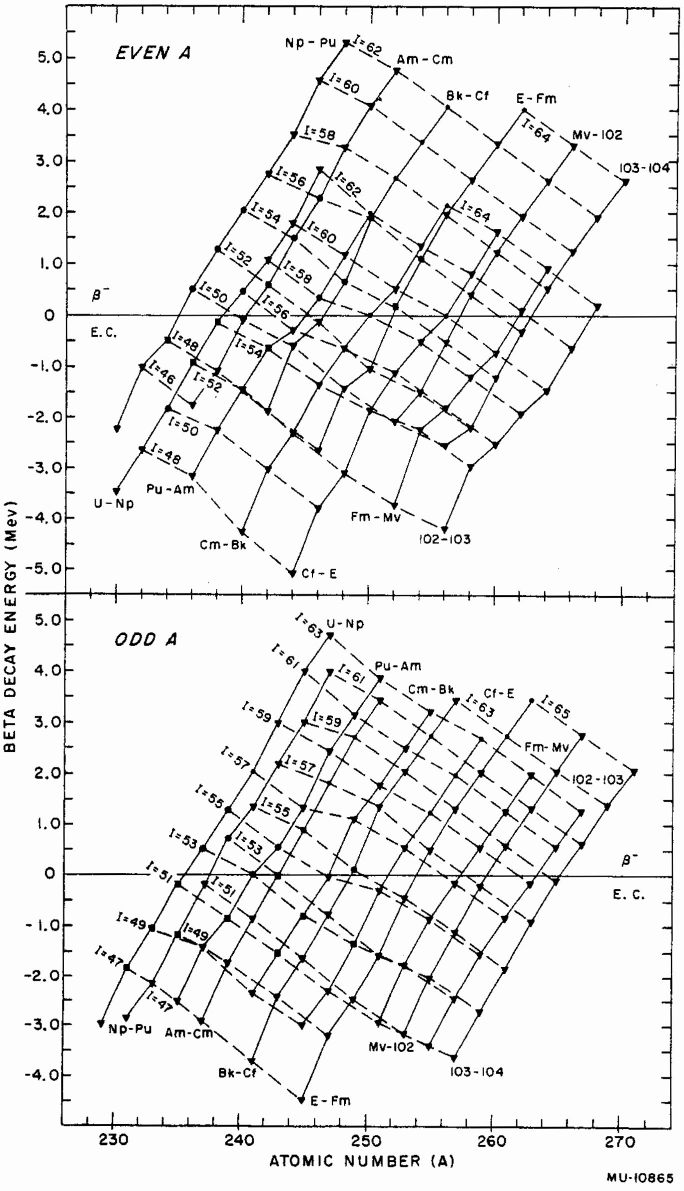
EVEN A
ODD A
BETA DECAY ENERGY (Mev)
ATOMIC NUMBER (A)
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
-3.0
-4.0
-5.0
230
240
250
260
270
β⁻
E.C.
Np - Pu
Am - Cm
Bk - Cf
E - Fm
Mv - 102
103 - 104
U - Np
Pu - Am
Cm - Bk
Cf - E
Fm - Mv
102 - 103
I=46
I=48
I=50
I=52
I=54
I=56
I=58
I=60
I=62
I=64
U - Np
Pu - Am
Cm - Bk
Cf - E
Fm - Mv
102 - 103
Np - Pu
Am - Cm
Bk - Cf
E - Fm
Mv - 102
103 - 104
I=47
I=49
I=51
I=53
I=55
I=57
I=59
I=61
I=63
I=65
MU-10865

Figure 39

Table 28. Beta-stable isotopes of transuranium elements.*

Neptunium	Np^{237}
Plutonium	Pu^{236}, Pu^{238}, Pu^{239}, Pu^{240}, Pu^{242}, Pu^{244}
Americium	Am^{241}, $\mathrm{Am}^{243}_{(?)}$
Curium	Cm^{242}, $\mathrm{Cm}^{243}_{(?)}$, Cm^{244}, Cm^{245}, Cm^{246}, $\mathrm{Cm}^{247}_{(?)}$, Cm^{248}, $\mathrm{Cm}^{250}_{(?)}$
Berkelium	None
Californium	Cf^{248}, Cf^{249}, Cf^{250}, Cf^{251}, Cf^{252}, Cf^{254}, $\mathrm{Cf}^{256}_{(?)}$
Einsteinium	E^{253}
Fermium	Fm^{252}, Fm^{254}, Fm^{255}, Fm^{256}, (Fm^{257}), (Fm^{258}) ($\mathrm{Fm}^{260}_{(?)}$), (Fm^{262}) (?)
Mendelevium	(Mv^{259})
102	(258), (260), (261), (262), (263), (264), (266)
103	(265)

* Parentheses enclose unknown isotopes predicted to be beta stable.

A question mark indicates an isotope for which the uncertainties in the data make it impossible to be sure of its beta stability.

63. Masses and binding energies. The energy data for the four mass types presented in Figures 34-37 can be interrelated and used to calculate the exact masses of all the transuranium isotopes provided that at least one mass is determined on an absolute scale and that certain neutron-binding energies are known. Since the most reliable and complete experimental data on absolute masses and on neutron binding energies are available in the region of lead, it is necessary to extend the closed decay-cycle plots to include isotopes in this region.

This has been done by Glass, Thompson and Seaborg[1] who then selected the following "best values" for neutron binding energies to interrelate the four mass types: $Pb^{206-207}$, 6.73 Mev; $Pb^{207-208}$, 7.38 Mev; and $Pb^{208-209}$, 3.87 Mev. These values were selected after considering data from certain nuclear reactions namely: (a) energy thresholds for reactions such as $Pb^{207}(\gamma, n)Pb^{206}$, (b) determination of the capture gamma-ray spectra in a reaction of the type $Pb^{207}(n, \gamma)Pb^{208}$, and (c) measurement of the deuteron and proton energies in a reaction like $Pb^{208}(d, p)Pb^{209}$.

The absolute masses of the nuclides then have been calculated from their energies relative to the absolute mass of Pb^{208} for which the values of 208.0410 ± 0.0015(10) and 208.0409 ± 0.0013(11) have been reported as a result of time-of-flight and magnetic mass spectrographic measurement, respectively. The value adopted for this compilation is 208.04100 (physical scale). In the table which follows this number of significant figures is carried throughout the calculations to be consistent with the relative accuracy of many of the energy values.

Additional quantities which enter into these mass calculations are the mass of the helium atom, 4.00387;(12) mass of the neutron 1.00898(12) and energy equivalent of mass, 931.2 Mev.[13] per atomic mass unit.

The method and the fundamental data outlined in the past few paragraphs were used to calculate the atomic mass values summarized in Table 29. In this table uncertain values are given in parentheses. Proton and neutron

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[10] P. I. Richards, E. E. Hays, and S. A. Goudsmit, Phys. Rev. 85, 630 (1952).

[11] G. S. Stanford, H. E. Duckworth, B. C. Hogg, and J. S. Geiger, Phys. Rev. 85, 1039 (1952).

binding energies were calculated for each isotope from the mass values using the value 1.00898 for the mass of the neutron and 1.00814 for the mass of the proton.[12] Values in Table 29 are slightly different from those given previously by Glass _et al_[1] reflecting the changes in the decay-energy cycles mentioned previously. Huizenga[14] has also provided a complete table of masses for the heavy element region. A general discussion of atomic masses is given by A. H. Wapstra in Volume 38 of the "Handbuch der Physik".

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[12] F. Ajzenberg and T. Lauritsen, Rev. Mod. Phys. _24_, 321 (1952).

[13] J. W. DuMond and E. R. Cohen, Rev. Mod. Phys. _25_, 691 (1953).

[14] J. R. Huizenga, Physica _21_, 410 (1955).

Table 29. Isotopic Masses (Physical Scale) and Binding Energies of Last Neutron and Last Proton (in Mev) for Isotopes of Transuranium Elements

92-Uranium	B_n	B_p
(226.09962)		(4.24)
227.10158	(6.54)	4.13
228.10195	8.02	5.00
229.10433	6.15	5.07
230.10527	7.48	5.40
231.10795	5.86	5.51
232.10911	7.29	6.14
233.11173	5.92	6.41
234.11343	6.77	6.56
235.11678	5.25	6.48
236.11884	6.44	7.06
237.12211	5.32	7.42
238.12458	6.06	(7.48)
239.12843	4.78	(7.58)
240.13106	5.91	(8.02)
(241.13514)	(4.57)	(7.98)
(242.13789)	(5.79)	(8.73)
(243.14291)	(3.69)	
(244.14549)	(5.96)	
(245.15130)	(2.96)	
(246.15433)	(4.53)	
(247.16076)	(2.38)	
93-Neptunium		
229.10753		2.39
230.10898	7.00	3.24
231.10991	7.50	3.26
232.11195	6.46	3.86
233.11285	7.53	4.10
93-Np(cont.)	B_n	B_p
234.11539	5.99	4.17
235.11696	6.90	4.30
236.11982	5.70	4.75
237.12155	6.75	5.06
238.12471	5.42	5.16
239.12628	6.18	5.28
240.13056	5.10	5.60
241.13295	6.14	5.83
(242.13674)	4.82	(6.08)
(243.13970)	5.61	(5.90)
(244.14358)	4.75	(6.96)
(245.14700)	5.18	(6.18)
(246.15129)	4.36	(7.58)
(247.15571)	4.25	(6.30)
(248.15971)	4.64	(8.56)
94-Plutonium		
(230.11138)		(3.99)
231.11299	(6.86)	3.85
232.11302	8.34	4.69
233.11517	6.36	4.59
234.11591	7.67	4.73
235.11822	6.21	4.95
236.11926	7.39	5.44
237.12175	6.05	5.79
238.12331	6.90	5.94
239.12705	5.60	6.12
240.12836	6.43	6.37
241.13150	5.44	6.71

94-Pu(cont.)	B_n	B_p
242.13380	6.21	6.78
243.13736	5.05	(7.01)
244.13984	6.05	(7.45)
(245.14378)	(4.70)	(7.40)
246.14638	(5.93)	(8.15)
(247.15143)	(3.66)	(7.45)
(248.15404)	(5.94)	(9.14)
(249.15965)	(3.14)	(7.64)
(250.16249)	(5.71)	
(251.16873)	(2.55)	
95-Americium		
(235.12093)		(2.90)
236.12268	(6.74)	3.43
237.12328	7.80	3.84
238.12573	6.08	3.87
239.12720	6.99	3.96
240.12990	5.85	4.21
241.13147	6.90	4.68
242.13449	5.55	4.79
243.13676	6.25	4.83
244.14017	5.19	4.97
245.14237	6.31	5.23
246.14599	4.99	(5.52)
(247.14882)	(5.72)	(5.31)
(248.15278)	(4.68)	(6.33)
(249.15626)	(5.12)	(5.51)
(250.16037)	(4.53)	(6.90)
(251.16458)	(4.45)	(5.64)
(252.16840)	(4.80)	(7.89)

96-Curium	B_n	B_p
(236.12459)		(4.18)
237.12644	(6.64)	4.08
238.12690	7.93	4.21
239.12907	6.34	4.47
240.12999	7.51	4.99
241.13239	6.13	5.27
242.13385	6.99	5.36
243.13676	5.66	5.47
244.13855	6.69	5.91
245.14140	5.71	6.43
246.14353	6.38	6.50
(247.14687)	(5.25)	(6.76)
(248.14927	(6.13)	(7.17)
(249.15333)	(4.58)	(7.07)
(250.15601)	(5.86)	(7.81)
(251.16088)	(3.83)	(7.11)
(252.16329)	(6.12)	(8.78)
(253.16872)	(3.31)	(7.29)
(254.17137)	(5.89)	
(255.17743)	(2.72)	
(256.17990)	(6.06)	
97-Berkelium		
(240.13460)		(2.44)
(241.13493)	(8.05)	(2.98)
(242.13710)	(6.34)	(3.19)
243.13841	(7.14)	3.34
244.14105	5.91	3.59
245.14226	7.23	4.13
246.14497	5.84	4.26

97-Bk (cont.)	B_n	B_p
247.14691	6.55	4.43
248.14997	5.52	(4.70)
249.15216	6.32	(4.89)
250.15601	4.77	(5.08)
(251.15898)	(5.60)	(4.82)
(252.16274)	(4.86)	(5.85)
(253.16604)	(5.29)	(5.02)
(254.16996)	(4.71)	(6.42)
(255.17398)	(4.62)	(5.15)
(256.17761)	(4.98)	(7.41)
(257.18220)	(4.09)	(5.44)
98-Californium		
(241.13894)		(3.54)
(242.13913)	(8.18)	(3.67)
243.14103	(6.59)	(3.92)
244.14169	7.75	4.53
245.14402	6.19	4.81
246.14509	7.36	4.94
247.14774	5.90	5.00
248.14926	6.95	5.40
249.15205	5.76	5.64
250.15397	6.57	5.89
(251.15753)	(5.05)	(6.17)
(252.15989)	(6.17)	(6.74)
(253.16386)	(4.66)	(6.54)
(254.16636)	(6.03)	(7.28)
(255.17104)	(4.01)	(6.58)
(256.17326)	(6.29)	(8.25)
(257.17850)	(3.49)	(6.76)
(258.18096)	(6.06)	(8.73)
(259.18683)	(2.90)	
(260.18912)	(6.23)	

99-Einsteinium	B_n	B_p
(244.14717)		(1.87)
(245.14726)	(8.28)	(2.40)
(246.14917)	(6.57)	(2.78)
247.15025	(7.36)	2.78
248.15259	6.19	3.07
249.15351	7.50	3.62
250.15596	6.08	3.94
251.15785	6.60	3.97
252.16109	5.35	(4.27)
253.16328	6.32	(4.42)
254.16691	4.98	(4.74)
(255.16969)	(5.77)	(4.48)
(256.17326)	(5.04)	(5.51)
(257.17637)	(5.47)	(4.69)
(258.18010)	(4.88)	(6.08)
(259.18393)	(4.80)	(4.82)
(260.18738)	(5.15)	(7.07)
(261.19179)	(4.26)	(5.10)
(262.19541)	(4.98)	
(263.20050)	(3.63)	
100-Fermium		
(245.15208)		(3.01)
(246.15202)	(8.41)	(3.14)
(247.15369)	(6.81)	(3.38)
(248.15410)	(7.98)	(4.00)
249.15620	(6.41)	4.22
250.15708	7.54	4.26
251.15955	6.06	4.24
252.16090	7.11	4.75
253.16376	5.70	5.10
254.16573	6.52	5.30
(255.16917)	(5.16)	(5.48)

100-Fm (cont.)	B_n	B_p
(256.17118)	(6.49)	(6.20)
(257.17498)	(4.83)	(5.99)
(258.17728)	(6.21)	(6.73)
(259.18176)	(4.19)	(6.04)
(260.18381)	(6.46)	(7.70)
(261.18885)	(3.67)	(6.22)
(262.19112)	(6.24)	(8.20)
(263.19680)	(3.07)	(6.29)
(264.19890)	(6.41)	(9.07)
101-Mendelevium		
(251.16274)		(2.31)
(252.16491)	(6.34)	(2.59)
(253.16566)	(7.67)	(3.15)
(254.16815)	(6.03)	(3.48)
(255.17010)	(6.55)	(3.51)
(256.17313)	(5.54)	(3.89)
(257.17515)	(6.49)	(3.89)
(258.17858)	(5.16)	(4.22)
(259.18118)	(5.94)	(3.95)
(260.18456)	(5.22)	(4.98)
(261.18748)	(5.64)	(4.16)
(262.19103)	(5.05)	(5.54)
(263.19468)	(4.97)	(4.27)
(264.19794)	(5.33)	(6.53)
(265.20217)	(4.42)	(4.58)
(266.20560)	(5.16)	
(267.21050)	(3.80)	
102		
(252.16716)		(3.47)
(253.16907)	(6.58)	(3.71)
(254.16977)	(7.71)	(3.75)

102 (cont.)	B_n	B_p
(255.17229)	(6.01)	(3.73)
(256.17369)	(7.06)	(4.24)
(257.17636)	(5.88)	(4.58)
(258.17815)	(6.69)	(4.78)
(259.18141)	(5.33)	(4.95)
(260.18324)	(6.66)	(5.67)
(261.18685)	(5.00)	(5.45)
(262.18896)	(6.39)	(6.20)
(263.19326)	(4.36)	(5.51)
(264.19512)	(6.63)	(7.17)
(265.19997)	(3.85)	(5.69)
(266.20206)	(6.41)	(7.68)
(267.20756)	(3.24)	(5.76)
(268.20948)	(6.58)	(8.54)
103		
(255.17599)		(1.79)
(256.17821)	(6.29)	(2.07)
(257.17901)	(7.62)	(2.63)
(258.18133)	(6.20)	(2.95)
(259.18309)	(6.72)	(2.98)
(260.18593)	(5.72)	(3.37)
(261.18775)	(6.67)	(3.38)
(262.19101)	(5.32)	(3.70)
(263.19343)	(6.11)	(3.42)
(264.19662)	(5.39)	(4.45)
(265.19937)	(5.81)	(3.63)
(266.20273)	(5.22)	(5.00)
(267.20620)	(5.14)	(3.73)
(268.20927)	(5.50)	(5.99)
(269.21333)	(4.59)	(4.00)
(270.21658)	(5.32)	
(271.22130)	(3.97)	

104	B_n	B_p	104 (cont.)	B_n	B_p
(256.18095)		(2.96)	(264.19606)	(6.83)	(5.14)
(257.18293)	(6.52)	(3.19)	(265.19949)	(5.17)	(4.92)
(258.18368)	(7.66)	(3.23)	(266.20141)	(6.56)	(5.67)
(259.18602)	(6.18)	(3.21)	(267.20553)	(4.53)	(4.98)
(260.18724)	(7.23)	(3.72)	(268.20721)	(6.80)	(6.64)
(261.18973)	(6.05)	(4.05)	(269.21188)	(4.02)	(5.16)
(262.19133)	(6.86)	(4.24)	(270.21377)	(6.59)	(7.16)
(263.19441)	(5.50)	(4.42)	(271.21909)	(3.41)	(5.25)

II. REGULARITIES IN THE RATE OF ALPHA DECAY AND IN THE ENERGY LEVELS OBSERVED IN ALPHA DECAY PROCESSES

64. The rate of alpha decay. A detailed discussion of alpha decay is beyond the scope of this article since this subject is covered by Rasmussen and Perlman in Volume 42 of the Handbuch der Physik. Hence, we shall review briefly only a few regularities pertaining to the transuranium element region.

The original formulation of the one-body theory of alpha decay by Gamow[15] and Condon and Guerney[16] which treats alpha decay as a simple quantum-mechanical, barrier-penetration problem accounts rather well in a general way for alpha disintegration rates which vary over the enormous range of 10^{24}. In recent years the large amount of new data which has appeared on artificially prepared isotopes has stimulated many authors to make detailed comparison of the data with various formulations of the Gamow theory. The principal fact emerging from these studies has been that if attention is restricted to ground-state transitions in even-even nuclei, the simple one body theory accounts with truly remarkable precision for the variation in half-life with atomic number and alpha decay energy.[16a]

A strictly empirical correlation of the data on even-even alpha emitters is given in Figure 40. In this figure the logarithm of the alpha half-life (corrected when necessary for branching decay by other decay modes) is plotted versus the alpha disintegration energy. It is seen that the data define a smooth family of curves. The curves in Figure 40 are theoretical, calculated according to Kaplan's[17] formulation of the rigorous equations of Preston[18] for the one-body theory. In making such calculations it is necessary to introduce a value for the nuclear radius, r_o. Kaplan found that the value $r_o = (1.57 \pm 0.015) A^{1/3} \times 10^{-13}$ cm when substituted in the equations for the decay constant λ gave the correct values for the even-even nuclei. Perlman and Asaro[19] have shown empirically that for the most precise agreement over the transuranium element range, it is necessary to allow for a steady decrease

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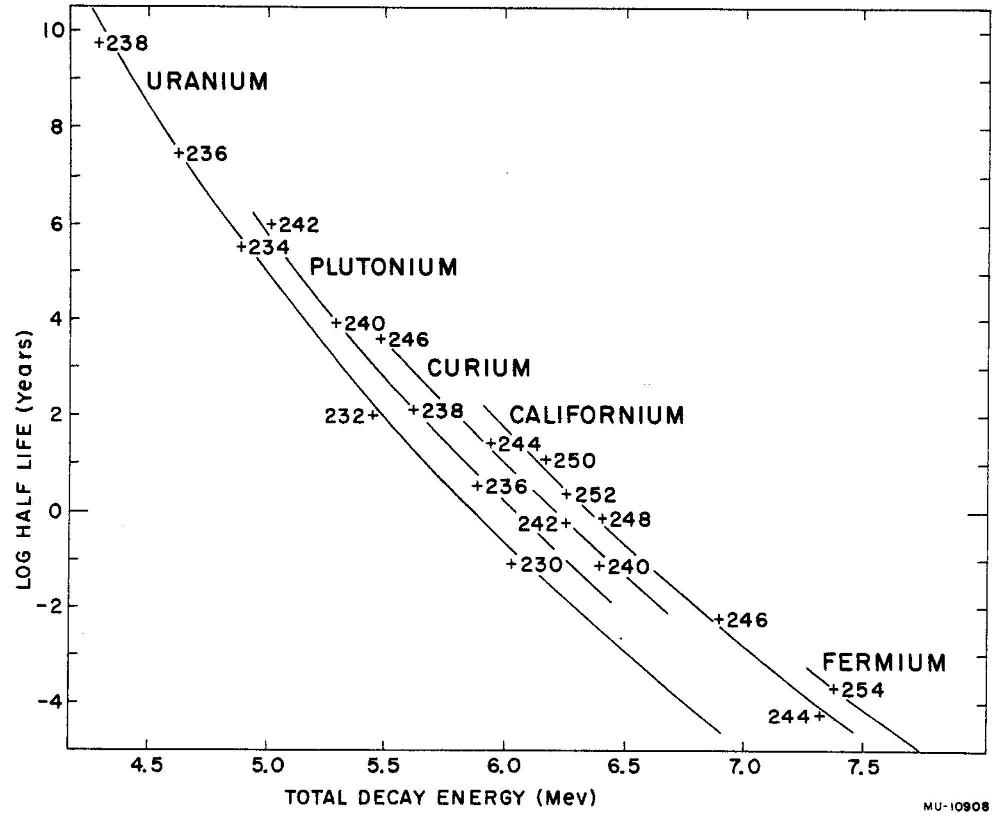
[15] G. Gamow, Z. Physik 51, 204 (1928).

[16] E. U. Condon and R. W. Gurney, Phys. Rev. 33, 127 (1929); Nature 122, 439 (1928).

[16a] I. Perlman, A. Ghiorso, and G. T. Seaborg, Phys. Rev. 77, 26 (1950).



10
8
6
4
2
0
-2
-4
LOG HALF LIFE (Years)
4.5
5.0
5.5
6.0
6.5
7.0
7.5
TOTAL DECAY ENERGY (Mev)
+238
URANIUM
+236
+242
+234
PLUTONIUM
+240
+246
CURIUM
232+
+238
CALIFORNIUM
+244
+250
+236
+252
242+
+248
+230
+240
+246
FERMIUM
+254
244+
MU-10908

Figure 40

in r_o as a function of Z amounting to a few precent in going from plutonium to fermium. It is possible then to account very well for the known alpha decay data on even-even transuranium element isotopes and to predict with considerable confidence the half-lives of unknown even-even isotopes. One other conclusion which follows from the strong dependence of the disintegration constant upon the energy is that the alpha transition leading to the ground state must be the most abundant transition. Experimentally, this is true in every case.

Figure 40. Half life of even-even isotopes versus alpha decay energy.

When isotopes with an odd number of neutrons or protons are considered it is found that the disintegration constants do not vary in the smooth manner predicted by the simple theory. In general the disintegrations constants are considerably longer than would be expected. Perlman et al[20] have introduced the term departure factor to give quantitative expression to this deviation. The departure factor (sometimes referred to as hindrance factor) is defined as the ratio of the observed partial half-life (for a specific alpha particle group) to the one calculated from the theory using the nuclear radius parameter obtained from a consideration of the even-even isotopes. Table 30 lists the calculated departure factors for ground-state alpha transitions in transuranium element isotopes containing odd nucleons. The chief facts to be noted are that the departure factor can be large and that the variation in departure factor follows no obvious pattern. Departure factors for transitions to excited levels in the daughter nucleus also vary erratically. It frequently happens that the alpha decay in odd-nucleon types goes more readily to excited levels than to the ground state in spite of the large dependence of alpha decay upon alpha particle energy. Hence, alpha spectra of odd nucleon types are more complex than those of even-even nuclei and in some instances the ground state transitions are not observed. Decay schemes of transuranium element alpha emitting isotopes were given previously in Figures 7, 11, 16, 24, 26, 28, 29

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[17] I. Kaplan, Phys. Rev. 81, 962 (1951).

[18] M. A. Preston, Phys. Rev. 71, 865 (1947).

[19] I Perlman and F. Asaro, Ann. Rev. Nucl. Sci. 4, 157 (1954).

Table 30. Departure factors for ground-state alpha transition of odd-nucleon isotopes

Alpha Emitter	Particle Energy	Abundance	Departure Factor
Cf^{249}	6.00	0.10	300
Bk^{245}	6.33	0.18	700
Bk^{243}	6.72	0.30	900
Cm^{243}	6.049	<0.5	$>$ 26
Am^{243}	5.341	<0.003	>1000
Am^{241}	5.535	0.0034	700
Pu^{241}	5.01	<0.11	$>$ 30
Pu^{239}	5.150	0.69	3
Np^{237}	4.86	<0.15	$>$ 50

and 32.

It is clear that some parameter or set of parameters not appearing in the simple one-body theory of alpha decay is operating powerfully to retard the emission of alpha particles. The effect of spin change has been considered and found to be incapable of explaining the results, at least in any manner in which spin change has been introduced so far. One suggestion[20] which has not received quantitative formulation has to do with the breakdown of the one-body model in its implication that alpha particles exist as discreet entities within the nucleus and that the probability of alpha-emission depends only upon the frequency factor of this preformed alpha particle in encountering the coulomb barrier and upon the rate of barrier penetration. In the case of odd-proton or odd-neutron isotopes it may be that a considerable delay is involved in

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[20] I. Perlman, A. Ghiorso, and G. T. Seaborg, Phys. Rev. 77, 26 (1950).

assembling the components of the alpha particle. Rasmussen[21] has discussed the suggestion in terms of the Bohr-Mottelson[22] nuclear model. In the case of the alpha decay of Am^{241} to Np^{237} both parent and daughter nuclei are known to have nuclear spin 5/2. The odd proton which gives rise to the 5/2 spin probably has a different wave function in the two cases; the necessity for a change in the state of this odd nucleon delays the alpha transition rate.

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[21] J. O. Rasmussen, Jr., Arkiv. för Fysik 7, (1953) No. 16.

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65. Energy level systematics in the decay of even-even alpha emitters. An examination of the decay schemes of the even-even isotopes of plutonium, curium, californium and fermium (see Figures 11, 24, 28, and 32) reveals a common pattern. The sequence of levels in the daughter nucleus reached by alpha decay have the spin and partiy designations 0+(ground), 2+, 4+, 6+, 8+ and the position of these levels above ground is approximately 45, 150, 300 and 510 Kev respectively. De-excitation of these levels is by a cascade of E2 gamma transitions with no cross over transitions. The electric quadrupole nature of these transitions have been characterized by measurement of absolute conversion coefficients, relative L subshell conversion coefficients, and α-γ angular correlations. The regularity of the pattern is evident from Table 31 which lists exact values for the energies of the 2+, 4+, and 6+ states.

The 2+ first excited state can be explained by modifications of the shell model of the nucleus or by the collective model of Bohr and Mottelson.[21] The collective model is particularly applicable to the transuranium elements as their isotopes appear in a region well removed from a closed shell. The theory predicts a rotational band of levels in which even states (0+, 2+, 4+. . .) appear for an even-even nucleus. The energy spacing of the levels should be proportional to $\frac{\hbar^2}{2\mathfrak{J}} I_j(I_j+1)$ where $\frac{\hbar^2}{2\mathfrak{J}}$ is the rotational energy quantum and I_j is the spin of the jth even state. This spacing agrees closely with the experimental values given in Table 31. A detailed comparison of the data with the predictions of the collective model makes it appear highly likely that the excited levels observed in alpha decay of even-even nuclei correspond to such rotational bands of levels.

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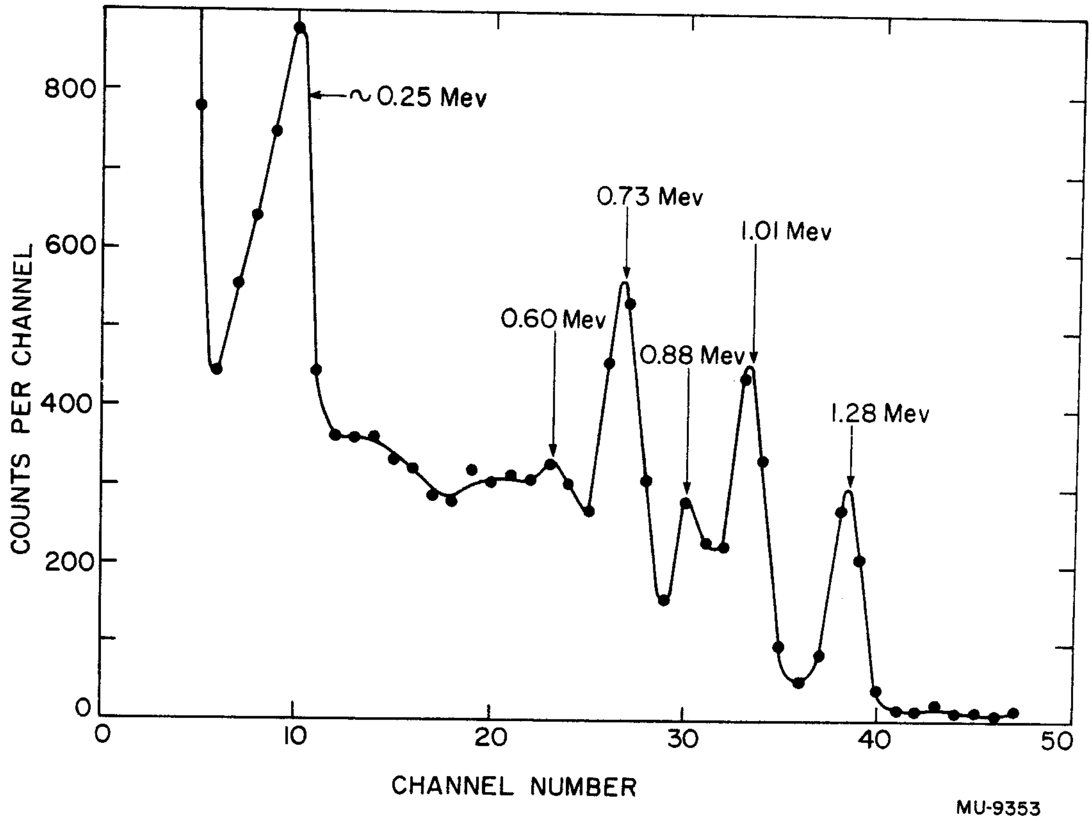
[22] A. Bohr and B. R. Mottelson, Dan Mat. fys. Medd. 27, No. 16 (1953) "Beta and Gamma Ray Spectroscopy", K. Siegbahn, Editor, Interscience Publishers, New York, 1955. Chapter 17.



~0.25 Mev
0.73 Mev
1.01 Mev
0.60 Mev
0.88 Mev
1.28 Mev
800
600
400
200
0
COUNTS PER CHANNEL
0
10
20
30
40
50
CHANNEL NUMBER
MU-9353

Figure 41

It has been noted that the percentage of transitions leading to these excited levels is less than can be accounted for by the energy dependence of alpha decay; i.e. the departure factor for alpha decay to these levels is greater than unity. This is most readily seen in Figure 41. Alpha transitions in even-even isotopes to the 2+ level are slightly but definitely hindered. Transitions to higher even states are hindered by quite large factors.

Figure 41. Departure factors in the alpha decay of even-even isotopes to excited even states in the daughter nucleus. From Perlman et al. University of California Radiation Laboratory Report UCRL-3068, July 1955, p. 39.

Odd parity excited states have been observed in the alpha decay of some even-even isotopes in addition to the even states. In the case of Th^{228} decay the well characterized 1^- level appears only 217 Kev above the ground state of the Ra^{224} daughter.[19] This may be the fundamental state of a rotational band of negative parity with associated 3^- and 5^- levels at 289 and 412 Kev, respectively.[23] Similarly in the decay of ionium, Th^{230} a rotational band of negative parity with levels 1^- (253 Kev) 3^-(320 Kev) and 5^-(445 Kev) is observed in addition to a 2+, 4+, 6+ level sequence at 68, 210 and 416 Kev respectively.[23]

Such odd parity states have been looked for in the transuranium element region, but only in the case of Cm^{242} has evidence for such a state appeared. In this case the assignment, 1^-, is given to a level at 605 Kev which is populated by alpha decay only to the extent 1×10^{-6}. Other high-lying odd parity states probably exist in the transuranium element region, but because of their location above the ground state they are reached in only an extremely small percentage of the alpha transitions and hence are extremely difficult to investigate.

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[23] F. Stephens, F. Asaro, and I. Perlman, unpublished results, University of California Radiation Laboratory, 1955.

Table 31. Energy in Kev of first three excited levels in daughter nucleus of even-even alpha emitters.

Alpha Emitter	Energy of 2+ Level	Energy of 4+ Level	Energy of 6+ Level
Pu^{236}	47	156	--
Pu^{238}	43.5	145	295
Pu^{240}	45	--	--
Cm^{242} *	44	146	301
Cm^{244}	42.9	142.7	293
Cf^{246}	42.3	145	294
Cf^{250}	42.9	--	--
Cf^{252}	43.4	144	--
Fm^{254}	42	136	--

* In the case of Cm^{242} a weak gamma ray of 210 Kev is believed to represent the 8+ ⟶ 6+ transition; the 8+ level is 513 Kev above ground.

66. Energy level systematics in the decay of odd nucleon alpha-emitters.

The alpha spectra of nuclei having an odd number of neutrons or protons are in general more complex than those of even-even nuclei and consequently have not been worked out with the same degree of certainty. Also as a group they show no common generalized pattern such as is the case for the even-even nuclei. The transition to the ground state is frequently highly hindered; in some cases it is not observed.

Nevertheless, some regularities are observable. In particular rotational bands of levels rather similar to those of the even-even nuclei have been identified. The principal difference is that the fundamental level of the rotational band is usually not the ground state in the case of odd-nucleon nuclei. For odd A nuclei the energies of rotational levels are given by the equation (valid except for $K = \Omega = 1/2$).

$$E_j = \frac{\hbar^2}{2\mathcal{J}} I_j(I_j+1) - I_o(I_o+1) \qquad (66.1)$$

where $\mathcal{J}$ = moment of inertia of surface wave motion.

I_j = nuclear spin of level j

I_o = spin of base level

Ω = component of total nucleonic angular momentum along the nuclear symmetry axis for the spheroidal nucleus

K = component of total angular momentum along the symmetry axis.

For odd A nuclei the quantum states representing collective rotational motion based on a given fundamental level I_o form the spin sequence

$$I = I_o,\ I_o+1,\ I_o+2,\ \ldots.$$

all with the parity of the fundamental level.

The level system for Np^{237} deduced from the alpha decay of Am^{241}, the beta decay of U^{237} and coulomb excitation experiments on Np^{237} is particularly interesting.[24, 25] Consider the level scheme shown in Figure 42 and the alpha decay scheme of Am^{241} given previously in Figure 16. Eighty-four percent of the Am^{241} alpha transitions go to a 59.57 Kev level in Np^{237}. This level has nuclear spin and parity $5/2^-$ and is the fundamental level of a rotational band with $\frac{\hbar^2}{2\mathcal{J}}$ = 6.19 Kev. The levels at 103.0 and 158.5 Kev with assignments 7/2- and 9/2- respectively are definitely members of this band. A level at ~ 227 Kev reported by Baranov and Shlyagin,[26] Goldin, et al[27] is probably the 11/2 - member of this band. It is reached by only 0.015 percent of the alpha transitions from Am^{241}.[27]

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[24] H. Jaffe, T. O. Passell, C. I. Browne, and I. Perlman, Phys. Rev. 97, 142 (1955).

[25] J M. Hollander, W. C. Smith, and J. O. Rasmussen, to be published, Phys. Rev. (1956); University of California Radiation Laboratory Report UCRL-3239, November 1955.

[26] S. A. Baranov and K. N. Shlyagin, Proceedings of Moscow meeting on Atomic Energy (July 1955) p. 252.

[27] L. L. Goldin, E. F. Tretyakov, G. I. Novikova, Proceedings of Moscow Meeting on Atomic Energy (July, 1955). pp. 226-249.

The ground state of Np^{237} has nuclear spin 5/2 but has opposite parity. The levels at 33.20 and at 76.1 Kev are believed to be members of a rotational band based on the ground state. Newton[28] has produced these levels by coulombic excitation of Np^{237}. The arrows pointing upward denote these excited transitions. The 76.1 Kev level has not been observed in the decay of Am^{241} or U^{237}. The spin sequence for this rotational band is 5/2+, 7/2+, and 9/2+ and the quantum of rotation $\frac{\hbar^2}{2\mathfrak{J}}$ is 4.75 Kev. The gamma transitions of Figure 42 have been well characterized where the transition type is indicated; these data are in agreement with the spin and parity assignments.

The low-lying levels of Np^{237} fall neatly into two rotational bands and indicate the essential correctness of the collective model in this mass region.

Figure 42. The energy levels of Np^{237}. (From Reference 25).

The low-lying levels of Np^{237} fall neatly into two rotational bands and indicate the essential correctness of the collective model in this mass region.

The alpha decay of Am^{243} to Np^{239} shows a pattern with considerable similarity to Am^{241} (See Figure 16). Eighty-seven percent of the alpha transitions go to a 75 Kev level in Np^{239} which probably is the fundamental level of a rotational band with spins 5/2, 7/2 and 9/2. The upper levels fall at 118 and 173 Kev respectively.

In a number of other cases it seems likely that series of levels will be proved to be associated with collective modes of nuclear motion. It is also probable that other important features of the spectra must bring in the concept of single particle states. Just what these states are and what guides the alpha-decay process to some and not to others are matters for future work.

III. NUCLEAR SPINS

Direct measurements of nuclear spin for the ground states of isotopes in the transuranium element region have been made in only six cases. These are summarized in Table 32.

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[28] J. O. Newton, Nature 175, 1028 (1955) and unpublished results, 1955.

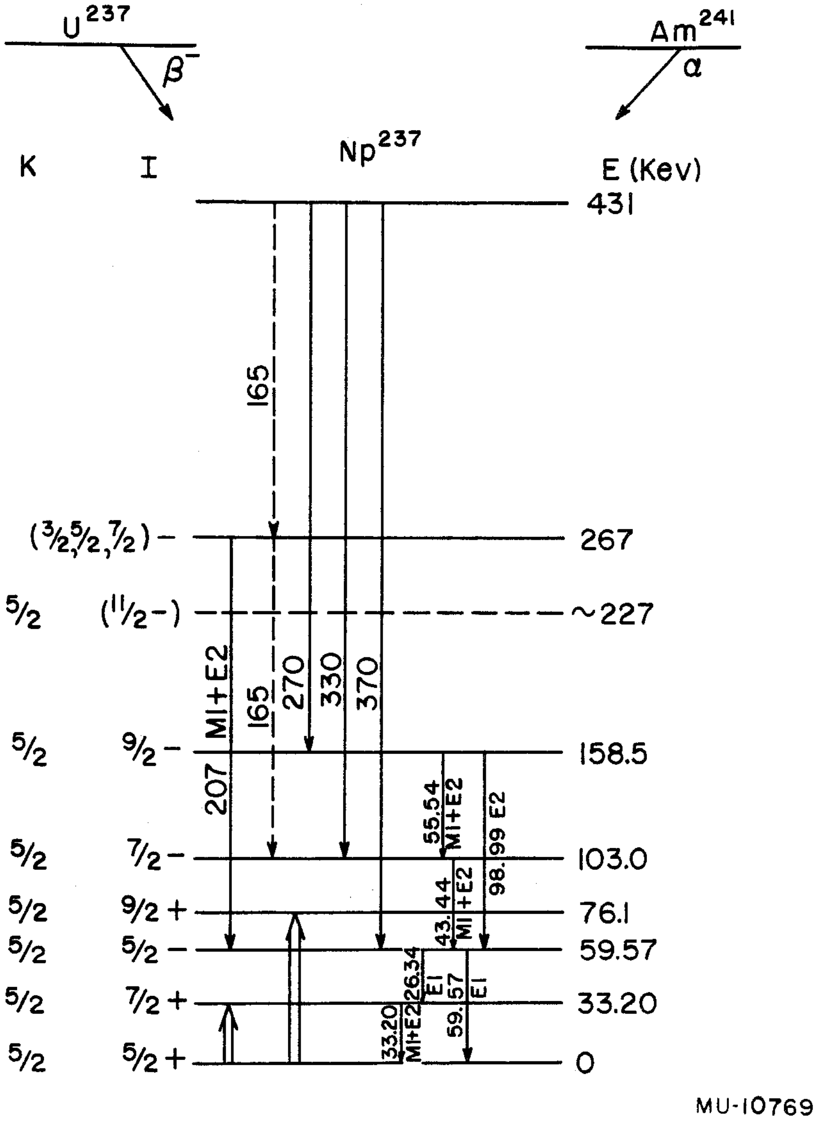
U237
β⁻
Am241
α
Np237
K
I
E (Kev)
431
165
(3/2,5/2,7/2) −
267
5/2
(11/2−)
~227
MI+E2
165
270
330
370
5/2
9/2 −
158.5
207
55.54
MI+E2
98.99 E2
5/2
7/2 −
103.0
43.44
MI+E2
5/2
9/2 +
76.1
5/2
5/2 −
59.57
26.34
E1
59.57
E1
5/2
7/2 +
33.20
33.20
MI+E2
5/2
5/2 +
0
MU-10769

Figure 42

Table 32. Determinations of nuclear spin in transuranium element region.

Isotope	Spin	Method	Reference
Np^{237}	5/2	hyperfine structure	F. S. Tomkins, Phys. Rev. 73, 1214 (1948)
	5/2	paramagnetic resonance	B. Bleaney, P. M. Llewellyn, M. H. L. Pryce, G. R. Hall, Phil. Mag. 45, 992 (1954).
Np^{239}	1/2	hyperfine structure	J. G. Conway, R. D. McLaughlin, Phys. Rev. 96, 541 (1954).
Pu^{239}	1/2	paramagnetic resonance	B. Bleaney, P. M. Lelwellyn, M. H. L. Pryce, G. R. Hall, Phil. Mag. 45, 773, (1954).
	1/2	hyperfine structure	M. van den Berg, P. F. A. Klinkenberg, Physica 20, 37, 461 (1954).
Pu^{241}	5/2	paramagnetic resonance	B. Bleaney, P. M. Lelwellyn, M. H. L. Pryce, G. R. Hall, Phil. Mag. 45, 991 (1954).
Am^{241}	5/2	hyperfine structure	M. S. Fred and F. S. Tomkins, Phys. Rev. 89, 318 (1953).
Am^{243}	5/2	hyperfine structure	J. G. Conway, R. D. McLaughlin, Phys. Rev. 94, 498 (1954).

IV. NEUTRON CROSS-SECTIONS AND SPONTANEOUS FISSION PROPERTIES

67. Neutron fission and capture cross-sections. Since nuclear fission is fully discussed by Wheeler in this volume, we shall not discuss that important subject here. The values for the slow neutron fission cross-sections and the neutron capture cross-sections of transuranium element isotopes are given in Table 33.

The fission cross-sections in almost every case were determined by fission counting in a double ionization chamber placed in the thermal column of a nuclear reactor. The sample to be measured was placed in one ionization chamber and a monitor sample containing a known amount of an isotope whose fission cross-section was accurately known was placed in the duplicate chamber. With present techniques this method is highly sensitive and accurate when samples of suitable isotopic purity are measured. The radiative capture cross-sections quoted in Table 33 were determined by activation methods using samples which were placed close to the reactor core where the neutron spectrum is not well known. In many cases the capture cross-sections were obtained as incidental information from experiments carried out principally for other purposes. Hence many of these values, particularly for the heaviest isotopes, are subject to revision.

Table 34 lists values of $\overline{\nu}$, the average number of neutrons released in fission; all except four of these values refer to spontaneous fission. Another important quantity is the multiplicity of neutrons from fission defined as the fraction of fissions producing 0, 1, 2, ... neutrons. Table 35 taken from the work of Hicks, Ise, and Pyle[29] shows the multiplicity of neutrons for the spontaneous fission of several isotopes. Hammel and Kephart[30] have made similar measurements on Pu^{240} and Diven, Martin, and Terrell[30a] have made measurements on a number of heavy isotopes.

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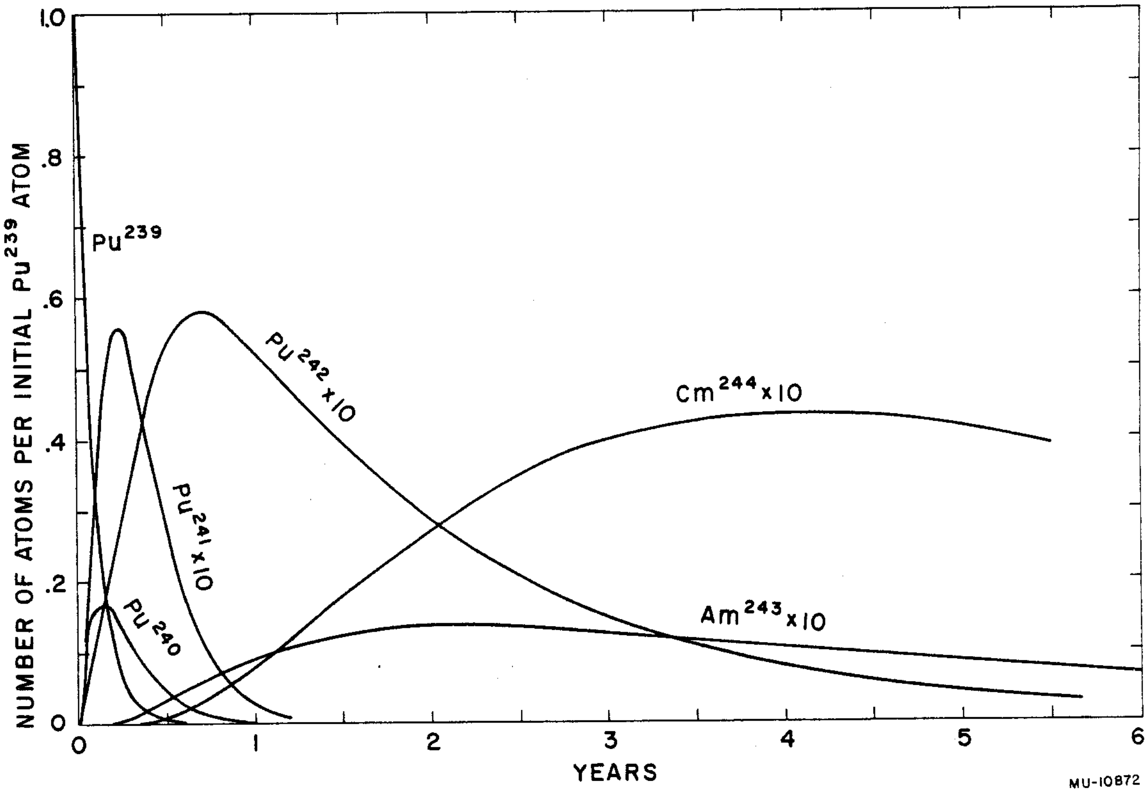
[29] D. A. Hicks, J. Ise, Jr., R. V. Pyle, University of California Radiation Laboratory Report UCRL-3146 Rev., November 1955; Phys. Rev., February 1, 1956.

[30] J. E. Hammel and J. F. Kephart, Phys. Rev. 100, 190 (1955).

[30a] Diven, Martin, and Terrell (in publication) Phys. Rev. February 1, 1956; see also R. B. Leachman Paper P/592 "Peaceful Uses of Atomic Energy-Proceedings of the Geneva Conference", United Nations, August 1955.



1.0
.8
.6
.4
.2
0
NUMBER OF ATOMS PER INITIAL Pu239 ATOM
Pu239
Pu240
Pu241 x 10
Pu242 x 10
Cm244 x 10
Am243 x 10
0
1
2
3
4
5
6
YEARS
MU-10872

Figure 43

In Sections 39 and 47 we described the preparation of americium and curium by intense neutron irradiation of plutonium. Figure 43 shows the changing composition of the heavy mass number isotopes as a function of time when small samples of Pu^{239} are irradiated at a flux of 3×10^{14} neutrons per cm^2 per second. The Pu^{239} is rapidly destroyed by fission and by neutron capture reactions. Figure 43 shows the buildup and destruction of the higher mass isotopes of plutonium and the eventual production of substantial amounts of Am^{243} and Cm^{244}.

Figure 43. Production of high mass isotopes by the irradiation of Pu^{239} at a flux of 3×10^{14} neutrons per cm^2 per second. The neutron capture and beta decay sequence is:

$$\begin{array}{ccccccccccccc}
\mathrm{Pu}^{239} & (n,\gamma) & \mathrm{Pu}^{240} & (n,\gamma) & \mathrm{Pu}^{241} & (n,\gamma) & \mathrm{Pu}^{242} & (n,\gamma) & \mathrm{Pu}^{243} & \xrightarrow{\beta^-} & \mathrm{Am}^{243} & (n,\gamma) & \mathrm{Am}^{244} \\
\downarrow & \sigma=385 & & \sigma=550 & \downarrow & \sigma=350 & & \sigma=68 & & & & \sigma=110 & \\
\sigma\mathrm{fiss}=765 & & & & \sigma\mathrm{fiss}=1100 & & & & & & \mathrm{Am}^{244} & \xrightarrow{\beta^-} & \mathrm{Cm}^{244}
\end{array}$$

In the case of a few transuranium element isotopes the value of the cross-sections for fission, for capture, or for inelastic scattering as a function of neutron energy have been determined with some care. The compilations of data on neutron cross-sections prepared by Hughes and Harvey[31] include such data for Np^{237}, Pu^{239}, Pu^{240}, Pu^{241}, and Am^{241}.

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[31] D. J. Hughes and J. A. Harvey "Neutron Cross-Sections", Brookhaven National Laboratory Report BNL-325, July 1955; Addendum to Report BNL-325, 'Heavy Element Cross-Sections", presented at Geneva, August 1955.

English work on the isotopes of uranium and plutonium is reviewed by Lynn and Pattenden[21a] and by Raffle and Price.[31a]

[31a] J. E. Lynn and N. J. Pattenden Paper P/423 and J. F. Raffle and B. T. Price Paper P/422 "Peaceful Uses of Atomic Energy- Proceedings of the Geneva Conference" United Nations, August, 1955.

Table 33. Slow neutron fission cross-sections and pile neutron radiative capture cross-sections for transuranium element isotopes

Isotope	σ Fission (Barns)	Ref.	σ Capture (Barns)	Ref.
Np^{234}	900 ± 300	1		
Np^{236} (5000 y)	2800	2		
Np^{237}	0.019 ± 0.003	3	170 ± 20	1, 4
Np^{238}	1600 ± 100	7		
Np^{239}	<3	8	80 ± 20	8
Pu^{238}	18 ± 2	9	455 ± 50 552 ± 7	13 10
Pu^{239}	750 ± 15	5	315 ± 16	5
	720	6		
Pu^{240}	<0.5	11	530 ± 50	11
Pu^{241}	1091 ± 87	12	350	11
	1100 ± 30	11, 26		
Pu^{242}	<0.3	11	68.2 ± 1	10
			30	14
Pu^{243}			170 ± 90	11
Pu^{244}			1.5 ± 0.3	11
Pu^{245}			260 ± 145	11
Am^{241}	3.2 ± 0.2	15	700 ± 200	5, 17, 18
	3.0	16		
Am^{242}	6000 *	17	2000	17
	2500	16	5500	16
Am^{242m}	3000	19		
	2000	17		
Am^{243}	<25	17, 16	137.5 ± 1.7	10
			115 ± 20	21
			140 ± 50	23
Cm^{242}	< 5	16	20 ± 10	20
Cm^{243}			250 ± 150	5
Cm^{244}			25 ± 10	21
Cm^{245}	1800 ± 300	11	200 ± 100	21

Isotope	σ Fission (Barns)	Ref.	σ Capture (Barns)	Ref.
Cm^{246}			15 ± 10	2
Cm^{247}			180	11
Cm^{248}			4	22
Bk^{249}			1100 ± 300	23
			350	24
Cf^{249}	630*	23	270 ± 100	23
Cf^{250}			~ 1500	24
Cf^{251}			~ 3000	24
Cf^{252}			25	24
			30	23
Cf^{254}			<2	23
$E^{253} \longrightarrow E^{254m}$			240 ± 100	27
			195	25
$E^{253} \longrightarrow E^{254}$			7	25
E^{254m}			<15	23
E^{254}	2000	25	40	25
E^{255}			30	25
Fm^{255}			<100	25

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*Pile neutrons

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Table 34. Average number of neutrons released in fission, $\bar{\nu}$

Isotope		Mode of Fission	Ref.
U^{233}	2.54 ± 0.04	n	1
	2.46 ± 0.15	n	10
U^{235}	2.46 ± 0.03	n	1
	2.45 ± 0.15	n	10
Pu^{236}	1.89 ± 0.20	sf	6
	2.30 ± 0.19	sf	2
Pu^{238}	2.04 ± 0.10	sf	6
	2.33 ± 0.08	sf	2
Pu^{239}	2.88 ± 0.04	n	1
	2.86 ± 0.18	n	10
Pu^{240}	2.257 ± 0.046	sf	5
	2.02 ± 0.11	sf	6
Pu^{241}	2.91 ± 0.10	n	4
	2.98 ± 0.21	n	10
Pu^{242}	2.26 ± 0.13	sf	6
	2.18 ± 0.09	sf	2
Cm^{242}	3.0 ± 0.3	sf	8
	2.65 ± 0.09	sf	2
	2.33 ± 0.10	sf	6
Cm^{244}	2.60 ± 0.12	sf	6
	2.84 ± 0.09	sf	2
Cf^{252}	3.82 ± 0.12	sf	2
	3.53 ± 0.15	sf	7
Fm^{254}	4.05 ± 0.19	sf	3

sf = spontaneous fission, n = slow neutron fission

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Table 35*

Calculated probabilities of emitting ν neutrons per spontaneous fission, P(ν), and the average number of neutrons per spontaneous fission, $\bar{\nu}$, based on $\bar{\nu}$ = 2.257 ± 0.046 for Pu^{240}

Pν	Pu^{236}	Pu^{238}	Pu^{240}	Pu^{242}	Cm^{242}	Cm^{244}	Cf^{252}
P_o	0.062 ± 0.035	0.044 ± 0.009	0.041 ± 0.009	0.063 ± 0.013	0.011 ± 0.005	0.001 ± 0.004	0.001 ± 0.001
P_1	0.156 ± 0.090	0.175 ± 0.026	0.219 ± 0.021	0.192 ± 0.034	0.126 ± 0.018	0.099 ± 0.017	0.021 ± 0.007
P_2	0.38 ± 0.13	0.384 ± 0.026	0.351 ± 0.021	0.351 ± 0.041	0.323 ± 0.018	0.281 ± 0.022	0.111 ± 0.019
P_3	0.28 ± 0.12	0.237 ± 0.027	0.241 ± 0.020	0.324 ± 0.047	0.347 ± 0.020	0.365 ± 0.018	0.271 ± 0.019
P_4	0.096 ± 0.086	0.124 ± 0.021	0.127 ± 0.018	0.033 ± 0.026	0.139 ± 0.013	0.198 ± 0.220	0.326 ± 0.018
P_5	0.033 ± 0.036	0.036 ± 0.009	0.020 ± 0.006	0.036 ± 0.013	0.050 ± 0.009	0.049 ± 0.009	0.178 ± 0.016
P_6			0.001 ± 0.002		0.004 ± 0.002	0.007 ± 0.002	0.077 ± 0.013
P_7					0.001 ± 0.001		0.013 ± 0.004
P_8							0.003 ± 0.001
$\bar{\nu}$	2.30 ± 0.19	2.33 ± 0.08	2.257 ± 0.046	2.18 ± 0.09	2.65 ± 0.09	2.84 ± 0.09	3.82 ± 0.12

*D. A. Hicks, J. Ise, Jr., and R. V. Pyle, Phys. Rev., Feb. 1, 1956.

68. Spontaneous fission. The experimental values of spontaneous fission half lives for heavy element isotopes are collected in Table 36. No adequate theory for the spontaneous fission process has been developed although a number of empirical observations and correlations have been presented.

An inspection of the table reveals a very strong dependence on atomic number, the process rapidly becoming more probable with increasing Z. A second striking fact is that nearly all the spontaneously fissionable nuclei are of the even-even nuclear type. Nuclei containing odd numbers of nucleons decay at a rate many factors of ten slower than do neighboring even-even nuclei. Whitehouse and Galbraith[32] and Seaborg[33] observed that the half lives showed an exponential dependence on Z^2/A. The rough validity of this relationship is shown in Figure 44 where the logarithm of the partial spontaneous fission half life is plotted against Z^2/A. With the accumulation of more data it became apparent that, although the parameter Z^2/A accounted in this manner broadly for the variation in half life over a range of Z values, for a given value of Z this parameter did not account for the variation of half life with the mass number, A. Huizenga[34] has pointed out that for a given value of Z the half life goes through a maximum as A varies. In figure 44 such a correlation is shown by drawing lines through the isotopes of each element. Similar graphs have been published by Fields and coworkers,[35] by Glass and coworkers,[36] and by Ghiorso.[37] Other correlations[38,39] involving the ratio of spontaneous fission to alpha half lives have also been useful for predictive purposes. Ghiorso[37] has noted that the spontaneous fission half lives for even-even isotopes containing more than 152 neutrons are considerably shorter than might be predicted even on the basis of a plot like that in Figure 44. In this figure, for example, the curve for the isotopes of californium drops off steeply on the high mass side. Ghiorso[37] tentatively relates this effect to a sub-shell closure at 152 neutrons.

Figure 44. Spontaneous fission half life versus Z^2/A

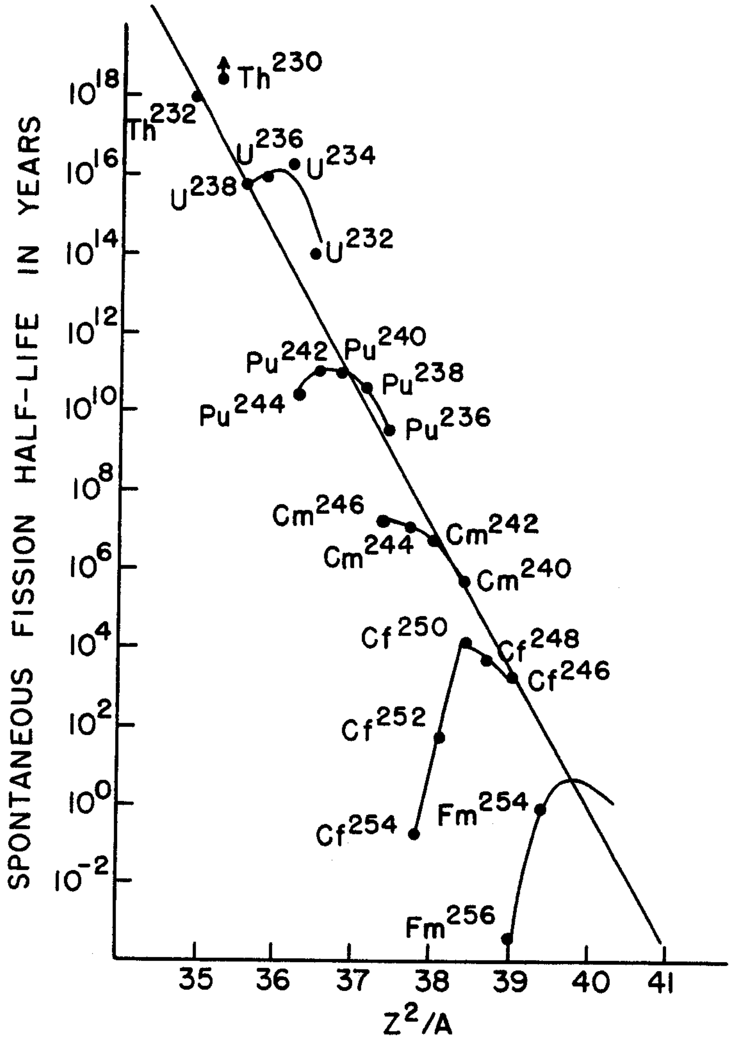

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Figure 44

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Spontaneous fission half lives are competitive with alpha decay half lives for the higher mass, even-even isotopes of californium and fermium and presumably for higher elements. Cf^{254} decays chiefly by spontaneous fission with a half life of 85 days; the alpha half life is expected to be about 100 years. In Fm^{256} the observed mode of decay is spontaneous fission; the observed half life of 3.5 hours is much shorter than the predicted alpha half life of about 10 days.

The rapid shortening of spontaneous fission lifetimes makes it unlikely that elements beyond fermium can be made in appreciable quantities by neutron irradiation techniques. According to figure 39 it is necessary to reach a mass number of 259 before a beta-emitting fermium isotope is reached. The spontaneous fission rates of Fm^{258} and Fm^{260} will be so large that most of the atoms of these isotopes will be destroyed by this process before they are converted to heavier isotopes by neutron capture. Hence very little buildup of element 101 and higher elements can be expected.

Fields et al.[35] and Bentley et al.[40] have discussed the possible usefulness of some of the short-lived spontaneously-fissioning isotopes as sources of neutrons. Cf^{252} is attractive for this purpose because it can be made in appreciable yield by long time irradiation of plutonium

(See Section 52.) This isotope has a neutron emission rate of 3×10^{12} neutrons per second per gram.

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Table 36. Half Lives for Spontaneous Fission

Isotope	Half Life	Reference
Th^{230}	$\geq 1.5 \times 10^{17}$ y	E. Segrè, Phys. Rev. 86, 21 (1952).
Th^{232}	$> 10^{20}$ y	A. V. Podgurskaya et al., Zhur. Eksptl. i Teoret. Fiz. 28, 503 (1955).
U^{232}	$8 \pm 5.5 \times 10^{13}$ y	A. H. Jaffey and A. Hirsch, unpublished work (1951).
U^{234}	1.6×10^{16} y	A. Ghiorso et al., Phys. Rev. 87, 163 (1952).
U^{235}	1.8×10^{17} y	E. Segrè, Phys. Rev. 86, 21 (1952)
U^{236}	2×10^{16} y	A. H. Jaffey and A. Hirsch, unpublished data (1949).
U^{238}	8×10^{15} y	E. Segrè, Phys. Rev. 86, 21 (1952)
Pu^{236}	3.5×10^{9} y	A. Ghiorso et al., Phys. Rev. 87, 163 (1952).
Pu^{238}	4.9×10^{10} y	A. H. Jaffey and A. Hirsch, unpublished data (1947).
Pu^{239}	5.5×10^{15} y	E. Segrè, Phys. Rev. 86, 21 (1952).
Pu^{240}	1.2×10^{11} y	O. Chamberlain et al., Phys. Rev. 94, 156 (1954).
	1.32×10^{11} y	E. M. Kinderman, Atomic Energy Commission Declassified Report HW-27660, April 1953.
Pu^{242}	$7.25 \pm 0.3 \times 10^{10}$ y	Unpublished results, Groups at Argonne National Laboratory and University of California Radiation Laboratory
Pu^{244}	$2.5 \pm 0.8 \times 10^{10}$ y	P. R. Fields et al., Phys. Rev. 100, 172 (1955).
Cm^{240}	1.9×10^{6} y	A. Ghiorso et al., Phys. Rev. 87, 163 (1952).
Cm^{242}	7.2×10^{6} y	A. Ghiorso and H. P. Robinson, unpublished results (1947); G. C. Hanna et al., Phys. Rev. 81, 466 (1951).

Table 36. Half Lives for Spontaneous Fission (Continued)

Isotope	Half Life	Reference
Cm^{244}	1.4×10^{7} y	A. Ghiorso et al., Phys. Rev. 87, 163 (1952).
Cm^{246}	3×10^{7} y	Unpublished results, Groups at Argonne National Laboratory and University of California Radiation Laboratory
Bk^{249}	6×10^{8} y	A. Ghiorso et al., unpublished results (1955).
	$> 2 \times 10^{8}$ y	L. B. Magnusson et al., Phys. Rev. 96, 1576 (1955).
Cf^{246}	$2.1 \pm 0.3 \times 10^{3}$ y	E. K. Hulet et al., Phys. Rev. 89, 878 (1953)
Cf^{248}	7×10^{3} y	E. K. Hulet, Ph.D. Thesis, University of California Unclassified Report UCRL-2283 (August 1953)
Cf^{249}	1.5×10^{9}	A. Ghiorso et al., unpublished results (1954).
Cf^{250}	$1.5 \pm 0.5 \times 10^{4}$ y	A. Ghiorso et al., Phys. Rev. 94, 1081 (1954); P. R. Fields et al., Nature 174, 265 (1954); L. B. Magnusson et al., Phys. Rev. 96, 1576 (1954)
Cf^{252}	66 ± 10 y	L. B. Magnusson et al.,Phys. Rev. 96, 1576 (1954); A. Ghiorso et al., Phys. Rev. 94, 1081 (1954)
Cf^{254}	85 ± 15 d	B. G. Harvey et al., Phys. Rev. 99, 337 (1955)
	60 ± 12 d	H. Diamond et al., Phys. Rev. 94, 1083 (1954)
E^{253}	3×10^{5} y	P. R. Fields et al., Phys. Rev. 94, 209 (1954); A. Ghiorso et al., unpublished results (1954)
E^{254}	1.5×10^{5} y	A. Ghiorso et al., unpublished results (1955)

Table 36. Half Lives for Spontaneous Fission (Continued)

Isotope	Half Life	Reference
Fm^{254}	200 d	G. R. Choppin et al., Phys. Rev. 94, 1080 (1954);
	220 ± 40 d	P. R. Fields et al., Phys. Rev. 94, 209 (1954)
Fm^{255}	> 60 y	A. Ghiorso et al., unpublished results (1955)
Fm^{256}	3 h	G. R. Choppin et al., Phys. Rev. 98, 1519 (1955)

y = years; d = days; h = hours.

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ACKNOWLEDGEMENTS

The authors wish to extend their thanks to Bruce M. Foreman, Jr., T. Darrah Thomas, and Mrs. Susanne Vandenbosch for valuable assistance in compiling data and to Miss Eileen Carson and Miss Jean Sansome for assistance in the preparation of the manuscript for publication.