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Charles S. Keller
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THE NEW ELEMENT CURIUM (ATOMIC NUMBER 96)

By Glenn T. Seaborg, Ralph A. James and Albert Ghiorso

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ABSTRACT

Two isotopes of the element with atomic number 96 have been produced by the helium-ion bombardment of plutonium. These isotopes are: (1) 96^{242} which emits alpha particles with a range 4.75 ± 0.1 cm in air (energy 6.1 Mev) and decays with a half-life of 5.0 ± 0.1 months; and (2) 96^{240} which emits alpha particles with a range of 4.95 ± 0.1 cm in air (energy 6.3 Mev) and decays with a half-life of 26.8 ± 0.3 days. 96^{242} has also been produced by neutron irradiation of 95^{241} . The mass assignments of these isotopes have been verified by isolation of their daughters, Pu^{238} and Pu^{236} . Some evidence for the isotope 96^{241} , decaying by orbital electron capture, is presented. The name curium, symbol Cm, is proposed for element 96. The chemical experiments indicate that the most stable oxidation state of curium is the III state.

A series of experiments has been carried out which has resulted in the first production and identification of isotopes of the element with atomic number 96. A brief description of these experiments and the radioactive and chemical properties of this element which have been deduced therefrom is given here.

A consideration of the methods by which isotopes of element 96 might be produced led to the use of two methods. The bombardment of plutonium with high energy helium ions should produce isotopes of this element. The neutron irradiation of Am^{241} (1) should lead to capture of neutrons and formation of Am^{242} which would decay by negative beta-particle emission to 96^{242} . Both of these methods were used in the present investigation and both led to the production of element 96.

It was of course expected that only minute (tracer) amounts of the new element would be formed and that identification would be possible

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only if the radioactive characteristics were favorable. Complete identification would depend upon showing by radiochemical techniques that the radioactivity resided in an element with unique chemical properties, different from all other known elements. It was necessary, in order to plan the chemical identification experiments, to have some idea as to the chemical properties of element 96 and for this purpose advantage was taken of some predictions of its chemical properties. The chemical investigation of the heaviest known elements (atomic numbers 89-92 inclusive) and the more recently discovered neptunium and plutonium, has led to the view that the heavy elements constitute a new "rare-earth" series in which the 5f electron shell is being filled and which formally begins with thorium. On this basis it was expected that element 96 would have a very stable III oxidation state with higher states being formed with great difficulty, if at all. Thus the anticipated chemical properties to be utilized for the isolation of detectable amounts of this element were to be those of elements with the typical III oxidation state such as the rare earths. It was essential to have at hand from the beginning a means for the complete chemical separation of the new element from plutonium, since the alpha-activity due to this element would be less than 1 ppm of that due to plutonium.

1. Experimental

The plutonium targets for cyclotron bombardment were prepared by the evaporation of plutonium nitrate solutions on grooved platinum plates, followed by mild ignition to form plutonium oxide. These targets were then bombarded directly in the target chamber of the cyclotron. There were two such bombardments in the 60-inch cyclotron of the University of California at Berkeley, the first one employing helium ions of 32 Mev energy,

and the second, helium ions with 40 Mev of energy:

Following the bombardments, the plutonium oxide was dissolved by the use of sulfuric acid, heating until extensive fumes of sulfur trioxide appeared, and then heating further to dryness. This was followed by the dissolution of the plutonium sulfate in dilute nitric acid and the remaining undissolved oxide was dissolved by heating with nitric acid, together with a small amount of added hydrofluoric acid.

On the assumption that the III oxidation state of element 96 would be present and would have an insoluble fluoride, lanthanum fluoride was precipitated from the solution after oxidizing the plutonium to the soluble VI oxidation state with 0.7 N nitric acid (in some experiments 0.1 N potassium dichromate was used with equally satisfactory results). The precipitate contained the beta-active rare earth fission product elements and presumably also contained any element 96 present in the III oxidation state. The precipitate was dissolved and the operation was repeated until all of the plutonium was eliminated. Although this procedure of necessity led to a concentration of a large amount of beta-activity due to the fission products along with the element 96, it was still possible to examine the alpha-activity which remained in this fraction.

At the beginning of the investigation the alpha-particles were identified as to range by means of absorption in very thin mica sheets placed immediately over the sample in an ordinary parallel plate ionization chamber. Later a multi-channel pulse analyzer was constructed and all subsequent energy measurements were made by employing it. With this instrument a thin sample is placed in an ionization chamber in which the total ionization of an alpha-particle can be measured as a voltage pulse. Individual pulses are sorted electronically and recorded on a number of

fast mechanical registers in such a way as to separate the individual alpha-particle energies in a mixture of alpha-emitters.

The neutron irradiation of the americium samples was made in the uranium-graphite chain reacting piles at the Clinton Laboratories and the Hanford Engineer Works. The samples irradiated in the Clinton pile were placed in the removable graphite stringer at the approximate center of the pile. In the Hanford pile the samples were inserted in the regular channels with graphite spacers between the sample cans and the uranium slugs.

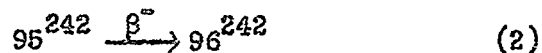
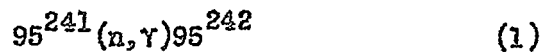
In the experiments in which the plutonium daughters were chemically separated after their growth as decay products from the isotopes of element 96, essentially the same method of chemical separation of plutonium from element 96 was used. In this case of course it was the oxidized plutonium which was recovered following the successive separation of lanthanum fluoride precipitates which removed the element 96.

2. Results

2.1 The Isotope 96^{242} . The helium-ion bombardment of plutonium led to the first definite identification (in July and August of 1944) of an isotope of element 96. In the first helium-ion bombardment about 10 mg of Pu^{239} was bombarded with helium ions of 32 Mev energy for a total of about 37 microampere-hours in the Berkeley 60-inch cyclotron. After the chemical separations described above, the rare earth fraction was found to contain about 500 disintegrations per minute of an alpha-activity with a range of about 4.75 ± 0.1 cm in air at 15° C and 760 mm of mercury pressure. This activity decayed with a half-life of five months (5.0 ± 0.1 months). The first isotopic assignment of this activity was to the isotope 96^{242} , formed in the reaction $Pu^{239}(\alpha, n)96^{242}$.

That this has now been confirmed to be the correct isotopic assignment will be made clear from the discussion of the remainder of the results of this investigation.

This same radioactivity was produced later (November and December, 1944) in a series of neutron bombardments of americium in which both bombardment time and total neutron exposure varied widely as a result of the use of the chain reacting piles at both Clinton and Hanford. In all of these neutron irradiations it was found that the ratio of the total intensity of the 4.75 cm alpha particles to that of the 4.05 cm alpha particles of Am^{241} varied approximately as the first power of the total neutron irradiation. The following sequence of nuclear reactions accounts for these observations:



The 4.75 cm alpha particles are due to the isotope ${}_{96}^{242}\text{Po}$. The decay rate here again corresponds to a half-life of five months so that this radioactivity agrees both in half-life and alpha-particle range with the ${}_{96}^{242}\text{Po}$ formed from the helium-ion bombardment of Pu^{239} .

The chemical evidence which allowed all previously known elements to be eliminated is as follows:

(1) The activity is carried quantitatively by lanthanum fluoride from solutions previously treated with various reducing and oxidizing agents ranging from zinc amalgam to argentic ion. The carrying is not influenced by the use of ammonium fluoride instead of hydrofluoric acid. This evidence alone eliminates all previously known elements except indium, lanthanum, and all of the rare earths, yttrium, actinium, thorium, and possibly protactinium.

(2) The activity is not precipitated with indium sulfide from acetic acid solution, thus eliminating indium.

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(3) Under the same conditions of acidity and concentration of reagents, the activity is not coprecipitated with ceric or zirconium iodates to as great an extent as are actinium, protactinium, and thorium, thus eliminating these last three elements and cerium.

(4) The activity can be partially separated from the rare earth yttrium subgroup by any one of three standard procedures: precipitation of the activity with lanthanum or praseodymium carrier from neutral to alkaline carbonate, oxalate, or formate solutions with yttrium, gadolinium, or lutetium holdback carrier.

(5) Europium can be separated by reduction to the II oxidation state with zinc amalgam and precipitation of EuSO_4 . The activity is not coprecipitated with europium under these conditions.

(6) Fractional separation from the remaining elements (lanthanum, praseodymium, neodymium, element 61, and samarium) can be achieved by the use of fluosilicate ion in solution during a partial precipitation of rare earth fluoride as carrier.

Confirmation of the isotopic assignment of the five months alpha-activity of 4.75 cm range came from a study of its decay-product. A sample containing about 2×10^6 disintegrations per minute of 96^{242} (produced by neutron irradiation of Am^{241}) was allowed to decay for about a month and at the end of this time the plutonium fraction was isolated and was found to consist of an alpha-activity with range 4.05 cm which can be ascribed to Pu^{238} . (2) The amount of Pu^{238} which grew was quantitatively determined in another experiment by addition of Pu^{239} tracer to establish the chemical loss during separation of the plutonium. The details of this experiment were as follows: A sample containing 1.293×10^6 c/m of 96^{242} was very carefully purified of all plutonium, 1102 counts/minute of Pu^{239} was then added and the sample allowed to stand for 70 days. At

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the end of that time the plutonium was separated from the element 96 and the ratio of Pu²³⁸ to Pu²³⁹ determined by pulse analysis (Fig. 1). < Fig. 1
The average of several such pulse analyses gave the value 1.45 for the ratio of Pu²³⁸ to Pu²³⁹. From these data and taking the half-life of ⁹⁶242 as 150 days, the half-life of Pu²³⁸ is calculated to be 92 ± 2 years, within the limit of error of the value obtained by Jaffey⁽³⁾ in direct decay measurements.

In addition to its alpha-particles ⁹⁶242 also emits a small amount of soft electromagnetic radiation and some electrons. Absorption curves of the radiations emitted by samples of ⁹⁶242 produced by neutron irradiation of Am²⁴¹ are shown in figures 2, 3, 4 and 5. The ⁹⁶242 in these samples < Figs. 2, 3, 4, and 5 was decontaminated from rare earth fission products by means of the fluosilicate procedure mentioned above and separated from americium by selective elution from a resin (Dowex 50) adsorption column.⁽⁴⁾ Samples from two different neutron irradiations of Am²⁴¹ differing by a factor of approximately 3 in total number of neutrons were measured and the absorption curves were found to be identical in all respects showing that (1) the radiations are not due to fission-product contamination since the two samples had radically different chemical histories and times of decay between removal from the pile and measurement of the radiations; and (2) that the radiations are actually due to ⁹⁶242 and not ⁹⁶243 or a higher mass isotope since, if they were due to ⁹⁶243, the level of activity would have been much higher in the sample which received longer irradiation. In addition to these curves it was found by means of bending the particles in a magnetic field that approximately 12% of the counts at zero absorber are due to low energy negative electrons. These radiations and their approximate abundances are summarized in Table 1.

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Table 1

Electromagnetic and Electron Radiations of 96^{242}

	Counts per 10^6 alpha disintegrations at 10% geometrical efficiency	Assumed counting efficiency	Number of events per disintegration
65 Kev Gamma ray	0.5	1%	1.8×10^{-3}
L x-rays	200	1.5%	0.15
Softer x-rays	100	--	--
Electrons	40	100%	4×10^{-4}

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2.2 The Isotope 96^{240} . In a second bombardment of Pu^{239} (March 1945) helium ions of energy 40 Mev were used to bombard 100 mg of Pu^{239} for 63.1 microampere-hours. A sample was treated by the same chemical procedure as already described and the final element 96 fraction contained about 2×10^5 alpha particle disintegrations per minute.

It was found that 20% of this activity was the 96^{242} activity described above while the remaining 80% was due to another alpha-emitter which emits alpha-particles with a range of 4.95 ± 0.1 cm in air at 15° C and 760 mm of mercury pressure. The over-all decay rate of this sample gave a half-life of about 1 month indicating that the half-life of the 4.95 cm range activity was somewhat less than one month and later resolution (Fig. 6) < Fig. 6 gave the value 26.8 days. This activity was thought to be due to either 96^{241} or 96^{240} produced by the reaction $Pu^{239}(\alpha, 2n)96^{241}$ or $Pu^{239}(\alpha, 3n)96^{240}$.

A sample of this activity was set aside and allowed to decay from the second to the fourth day after shut-down of the cyclotron. The plutonium fraction was then isolated and the pulse analysis curve (Fig. 7a) < Figs. 7a and 7b as well as the alpha decay curve (Fig. 7b) of this plutonium sample gave definite evidence of Pu^{236} whose radioactive properties had been definitely established. (5) The element 96 fraction was then allowed to grow plutonium again (77 days of growth) and the amount of Pu^{236} which had grown was quantitatively determined by the addition of Pu^{239} tracer to establish the chemical loss in the process of separation of the plutonium from the element 96. The additional details of this experiment which allowed a calculation of the half-life of the element 96 parent were as follows: 1.38×10^5 alpha counts/minute of the $96^{242} - 96^{240}$ mixture of which initially 70.2% were due to 96^{240} decayed for 77 days. At the end of that time the plutonium fraction was isolated after addition of 1935 counts per minute of Pu^{239} and the resulting plutonium sample pulse analyzed.

The average of several such pulse analyses (see Fig. 8) gave 1.14 as the value of the ratio of Pu^{236} to Pu^{239} . Using the value 983 days (obtained from figure 7b) for the half-life of Pu^{236} one calculates 26.7 days as the half-life of 96^{240} which is in excellent agreement with the value 26.8 days obtained by resolution of the alpha decay curve (Figure 6). < Fig. 8

2.3 Other Isotopes of Element 96. In addition to the isotopes 96^{240} and 96^{242} one other activity has been observed which may be due to either an isotope of element 96 or to an americium (element 95) isotope.

When the Geiger counter activity of the combined americium-element 96 fraction of plutonium targets bombarded with helium ions is followed with various absorbers the decay curves shown in figures 9, 10 and 11 are obtained. From the percentage of the alpha-activity in the sample which is due to 96^{242} the Geiger counter activity due to this isotope can be obtained from figures 2, 3, 4, and 5. If this is done it is found that there remains, in addition to an activity corresponding to the 96^{240} half-life, an activity of about 55 day half-life and one of about 2 day half-life. The ca. 2 day activity is very probably the same activity as the one which has been found in deuteron bombardments of Pu^{239} (1), i.e. the 50-hour Am^{238} . The 55 day activity has a large amount of soft-electromagnetic radiation, perhaps some electrons, but no hard gamma rays. It is probable that the activity is due to 96^{241} decaying by orbital electron capture. < Figs. 9, 10 and 11

3. Name for Element 96.

As the name for the element of atomic number 96 we should like to propose "curium", with symbol Cm. The evidence indicates that element 96 contains seven 5f electrons and is thus analogous to the element gadolinium, with its seven 4f electrons in the regular rare earth series. On this

basis element 96 is named after the Curie's in a manner analogous to the naming of gadolinium, in which the chemist Gadolin was honored.

It is a pleasure to acknowledge the help and cooperation of Dr. J. G. Hamilton and his group who rebuilt the Berkeley 60-inch cyclotron in order to make much of this work possible and who performed the bombardments. The cooperation of the groups at the Clinton Laboratories and the Hanford Engineer Works in making the neutron irradiations is also gratefully acknowledged.

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