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THE NEW ELEMENT BERKELIUM (ATOMIC NUMBER 97)

Stanley G. Thompson, Albert Ghiorso, and Glenn T. Seaborg

April 26, 1950

Berkeley, California

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THE NEW ELEMENT BERKELIUM (ATOMIC NUMBER 97)

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ABSTRACT

An isotope of the element with atomic number 97 has been discovered as a product of the helium-ion bombardment of americium. This isotope decays with the emission of alpha-particles of maximum energy 6.72 Mev (30 percent) and it emits lower energy alpha-particles of energies 6.55 Mev (53 percent) and 6.20 Mev (17 percent). The half-life of this isotope is 4.6 hours and it decays primarily by electron capture with about 0.1 percent branching decay by alpha-particle emission. The mass number is probably 243 as indicated by chemical separation of the alpha-particle and electron-capture daughters. The name berkelium, symbol Bk, is proposed for element 97.

The chemical separation of element 97 from the target material and other reaction products was made by combinations of precipitation and ion exchange adsorption methods making use of its anticipated (III) and (IV) oxidation states and its position as a member of the actinide transition series. The distinctive chemical properties made use of in its separation and the equally distinctive decay properties of the particular isotope constitute the principal evidence for the new element.

INTRODUCTION

The transuranium elements number 96, curium, and 95, americium, were discovered in 1944, the first by Seaborg, James, and Ghiorso,[1] the second by Seaborg, James, and Morgan.[2] The search for transcurium elements was begun by us in the fall of 1945. It was anticipated[3] that element 97 as ekaterbium in the actinide transition series would possess oxidation states (III) and (IV) with properties similar to curium in the (III) oxidation state and to plutonium (IV) in its (IV) oxidation state. It was more difficult to estimate the oxidation potential of the (III) → (IV) couple but it was expected that element 97 would be somewhat easier to oxidize than terbium (III) which is not oxidizable to higher states in aqueous solution at all. The salient point is that if element 97 could not be converted to an oxidation state higher than (III) in solutions it would be extremely difficult to separate in a short period of time from rare earth elements and from the actinide elements from which it must be produced. Americium is very difficult and curium probably impossible to oxidize above the (III) state in aqueous solution.[3] In other words, it appeared that it might be necessary to use tedious rare earth separations in order to separate and identify the new element, the isotopes of which do not exist in nature and whose neutron-deficient isotopes as produced by alpha-particle and deuteron bombardments would have short half-lives as a result of considerable instability towards alpha-particle emission and electron-capture decay.

In view of the fact that sufficiently intense beams of energetic particles of nuclear charge greater than two have never been available, it is obvious that

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[1] G. T. Seaborg, R. A. James, and A. Ghiorso, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 22.2 (McGraw-Hill Book Co., Inc., New York, 1949).

[2] Seaborg, James, and Morgan, ibid., Paper No. 22.1.

[3] Seaborg, Nucleonics 5, No. 5, 16 (1949).

there were only two methods of approach to the production of element 97. The first approach was through the bombardment of americium with helium ions or bombardment of curium with deuterons or helium ions. The second (not yet successful) was through intensive neutron irradiations of curium in order to eventually produce through successive (n,γ) reactions a curium isotope of mass sufficient to be unstable toward negative beta-particle decay and so produce an isotope of element 97.

Both methods were employed in attempting to observe element 97 and for each, different chemical procedures were used. Some of these procedures were designed to separate the new element in oxidation states greater than (III) and others were used on the assumption that element 97 existed in solution under most conditions in the tripositive oxidation state.

Although the broad assumptions made when the work was started were all correct, the experiments done prior to December, 1949 were unsuccessful for many reasons which may be grouped into three classes. First, the methods of predicting the properties of the new isotopes were relatively undeveloped and the experiments were never done with sufficient speed. The further development of the alpha-decay systematics[4] made it possible to estimate energies and half-lives for alpha-particle decay. The resulting estimated alpha-particle decay energies could be used in calculating by closed decay cycles the total energies for electron-capture decay or beta-particle decay. An empirical method of estimating electron-capture half-lives from disintegration energies was also developed[5] which, although very rough due to uncertainties in the degree of prohibition of this mode of decay in any given case, was very useful in making half-life estimates.

The second major difficulty was that of obtaining sufficiently large amounts of americium and curium as sources for the production of element 97. Eventually

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[4] Perlman, Ghiorso, and Seaborg, Phys. Rev. 77, 26 (1950).

[5] S. G. Thompson, Phys. Rev. 76, 319 (1949).

americium became available in milligram amounts by neutron irradiation of plutonium.[6] The isolation of the americium from the plutonium required tedious chemical procedures. The curium was produced in smaller amounts by the irradiation of americium with neutrons.[2,6]

The intense radioactivity of the americium and curium source materials presented the third major difficulty. This radioactivity necessitated not only the design and development of advanced techniques and equipment[7] for its safe handling, but also made it necessary to attain enormous separation factors in the isolation of the new element from the target material in order to be able to detect the small amounts of radioactivity due to it. Furthermore, this high degree of separation had to be carried out in good yield in a short length of time.

Essentially three chemical steps were developed to solve these chemical problems. The conversion of the americium to a hexapositive oxidation state[8] was used in the rapid removal of the bulk of the bombarded americium. An ion exchange method involving the separation of the actinide elements as a group from the rare earth fission products by elution with concentrated HCl[9] from a cation exchange column was exploited for the rapid separation of the tripositive actinide elements. An ion exchange method involving elution from a cation exchange resin at elevated temperature with ammonium citrate solution was used in the rapid separation of the tripositive actinide elements from each other. These steps had been worked out adequately by December, 1949 and the first successful experiment was done on December 19, 1949, as recently reported in a preliminary fashion.[10] Three successful

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[6] Ghiorso, James, Morgan, and Seaborg, Phys. Rev. (in press), May 1, 1950.

[7] Nelson Garden and co-workers, unpublished work.

[8] Asprey, Stephanou, and Penneman, J. Am. Chem. Soc. 72, 1425 (1950).

[9] K. Street, Jr. and G. T. Seaborg, J. Am. Chem. Soc. (to be published).

[10] Thompson, Ghiorso, and Seaborg, Phys. Rev. 77, 838 (1950).

confirmatory experiments were completed by February 15, 1950. For convenience of expression the name berkelium, symbol Bk, will be employed in the following discussion. The reasons for suggesting this name will be made clear at the end of the paper.

EXPERIMENTAL METHODS

Extraction of Americium

The Am^{241} used as target material for the production of element 97 was separated from strongly neutron-irradiated plutonium into which it grew as the daughter of the beta-particle decay of ~10-yr. Pu^{241}. The isotope Pu^{241} is produced[6] by the reactions $Pu^{239}(n,\gamma)Pu^{240}(n,\gamma)Pu^{241}$. The americium was separated and purified by combinations of precipitation and ion exchange methods.

Preparation and Bombardment of Targets

The americium targets were prepared for bombardment in the Crocker Laboratory 60-inch cyclotron by the evaporation of americium nitrate solutions in small platinum dishes of ~0.5-cm^2 area followed by ignition to form black americium oxide. The americium used was of ≈96 percent chemical purity as determined by spectrographic analysis. The major impurities were sodium (~1.5 percent), zinc (~1 percent), calcium (0.2 percent), aluminum (0.5 percent) and titanium (0.2 percent). These targets were placed inside a special target assembly, indicated schematically in Fig. 1, which was designed to prevent alpha-radioactivity from entering the cyclotron and to eliminate its spread to the surroundings during transportation. In this assembly the particle beam from the cyclotron was passed through two thin duralumin foils (each 1.5 mil in thickness) before entering the evacuated compartment containing the sample, and the compartment was isolated from the surroundings. The beam was also passed through a thin platinum foil placed directly in contact with and over the target dish. The

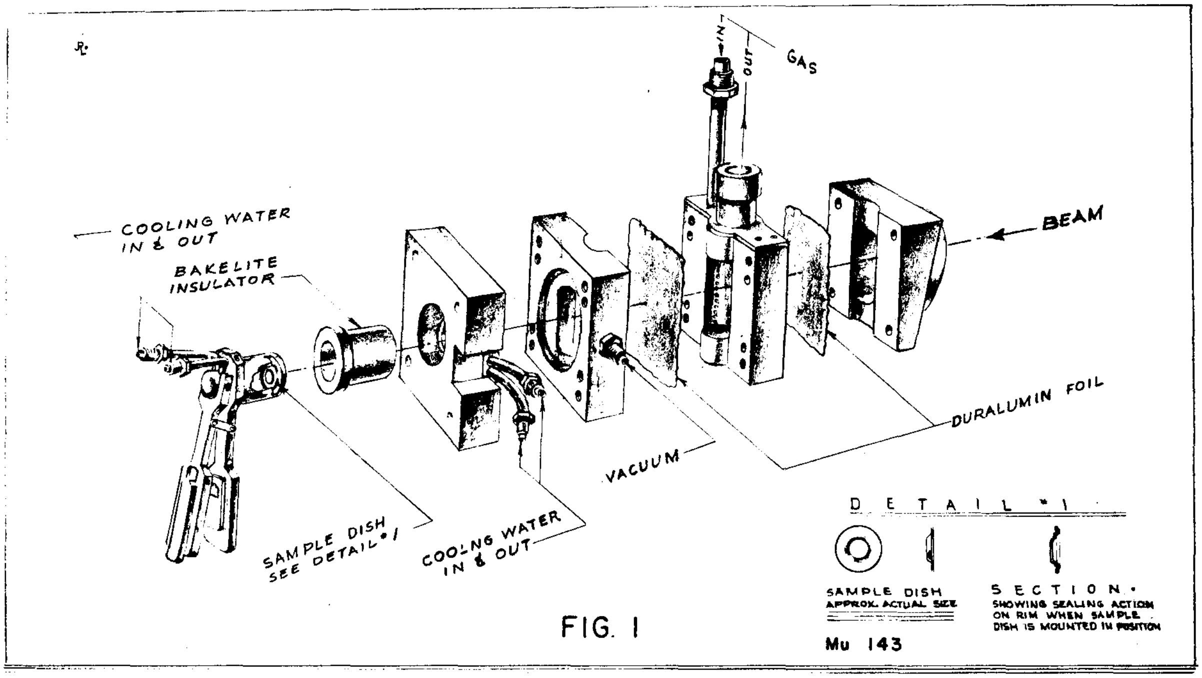

FIG. I

Fig. 1. Schematic sketch of the special target assembly for the bombardment of Am^{241} with helium ions in the 60-inch cyclotron. The radioactivity is prevented from entering the cyclotron and is safely confined during transportation.

thickness of this foil was changed to vary the energy of the particles (initial energy ~40 Mev). The duralumin foils reduced the energy to ~37 Mev and the 0.5-mil platinum foil further reduced it to ~35 Mev. This platinum foil also served to reduce the spread of radioactivity through the evacuated compartment. The back of the platinum dish containing the sample was cooled directly with a water jet. The intensity of the beam of helium ions striking the sample was determined by measuring the charge accumulated on the insulated target dish and foil. The energies of the helium ions were calculated as ranging from 30 to 35 Mev in various bombardments. (The intensity of the bombardments averaged about 2 microamperes per sq cm and the time of bombardment was usually about 6 hours.)

Chemical Procedure

Following the bombardments, the platinum dish containing the sample was removed to a gloved box (illustrated in Fig. 2) and the americium oxide dissolved in 6<u>M</u> nitric acid with heating (~75°C). Americium hydroxide was precipitated with the addition of excess ammonium hydroxide and separated by centrifugation. The hydroxide was dissolved in dilute (0.1<u>M</u>) HNO_3, the solution was made 0.2<u>M</u> in ammonium persulfate and 0.2<u>M</u> in ammonium sulfate and the americium converted to the hexapositive (fluoride-soluble) oxidation state by heating (in the case of the best results) for about 1-1/2 hours at 75°C. The major part of the americium was separated early in this manner in order to reduce the bulk of material with the berkelium and make possible the use of resin columns of smaller diameter. Although not absolutely necessary, this improves the sharpness and speed of the chemical separations. Unoxidized americium was precipitated by the addition of hydrofluoric acid (3<u>M</u>), the insoluble americium (III) fluoride carrying with it curium, element 97, and some - mostly rare earth - fission products. The fluoride precipitate was converted to a hydroxide by treatment with 6<u>M</u> KOH followed by centrifuging and washing. The hydroxide precipitate was

Fig. 2. Photograph of the gloved box in which the initial chemical separations of element 97 were made. Negative pressure in the box and the use of rubber gloves insures that no radioactivity escapes to the surroundings.

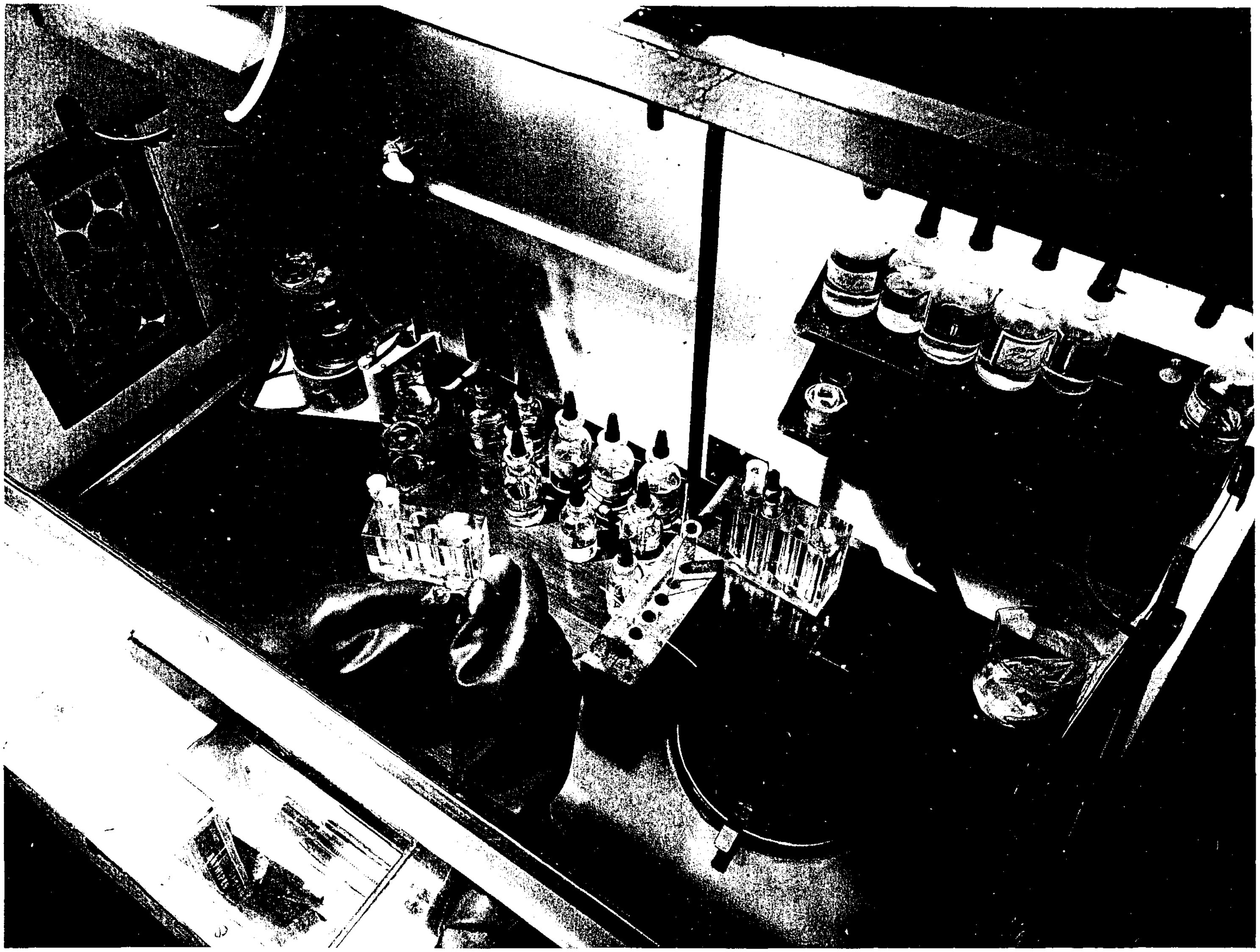

FIG. 2

dissolved in dilute perchloric acid (0.5$\underline{M}$) and the mixture of radioactivities was adsorbed on a small amount of ammonium form Dowex-50 resin* (spherical fines) which was then transferred to a 20 cm length, 2 mm diameter column packed with the same resin (refer to Fig. 3). The column was surrounded by a vapor jacket through which passed trichloroethylene vapor to maintain the temperature at about 87°C. The elution was performed by passing ammonium citrate (buffered with citric acid to pH 3.5 - total citrate concentration 0.25$\underline{M}$) through the column at a rate of 1 drop (~0.030 cm^3) about every two minutes and the drops were collected separately. (The element 97 fractions were usually collected in drops 35-40, and for comparison curium was collected in drops 60-65. The element 97 position is between terbium and gadolinium on these columns.) In order to separate the element 97 which was being sought from residual rare earth fission products, the citrate fractions in which it was present were combined and made acidic by the addition of HCl. The activity was adsorbed on Dowex-50 resin and transferred to a ~7 cm length column packed with Dowex-50 resin (hydrogen form)(refer to Fig. 4). Berkelium was then removed from the column more rapidly than the lanthanide elements by elution with 13$\underline{M}$ HCl, which forms stronger complex ions with tripositive actinide elements than it does with rare earth elements.[9] In the first successful search for element 97, the column employing hydrochloric acid for elution was used first for separation of the actinide elements as a group from the rare earth elements before using the column in which elution is performed with citrate to separate the individual actinide elements, thus making it possible to look for electron and electromagnetic radiations as well as alpha-radioactivity. In this case the excess hydrochloric acid was removed from the actinide fraction elutriant solution by rapid evaporation of the solution in the presence of an air jet. The berkelium separated in either manner was carrier-free and could be evaporated directly on platinum plates for counting purposes. Ignition of the plates to

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*Dow Chemical Company, Midland, Michigan.

Fig. 3. Jacketed Dowex-50 resin column used for the separation of element 97 from other actinide elements. Trichlorethylene vapor is passed through the jacket to maintain a high temperature (87°C) which increases the speed with which good separations can be made.

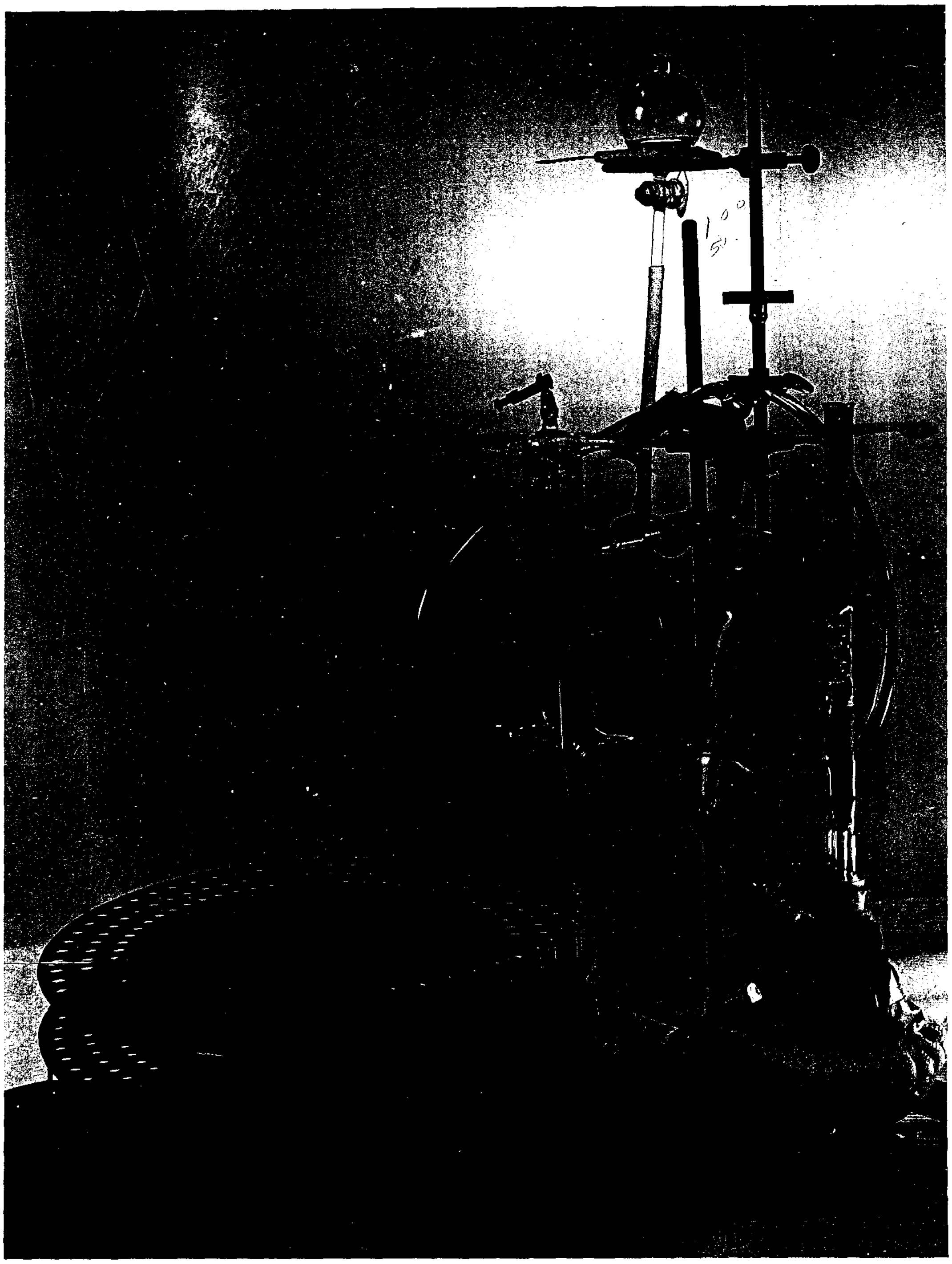

FIG. 3

Fig. 4. Dowex-50 (hydrogen form) resin column used for the separation of element 97 from rare earth isotopes. Concentrated (13M) hydrochloric acid removes element 97 and actinides more rapidly than rare earths.

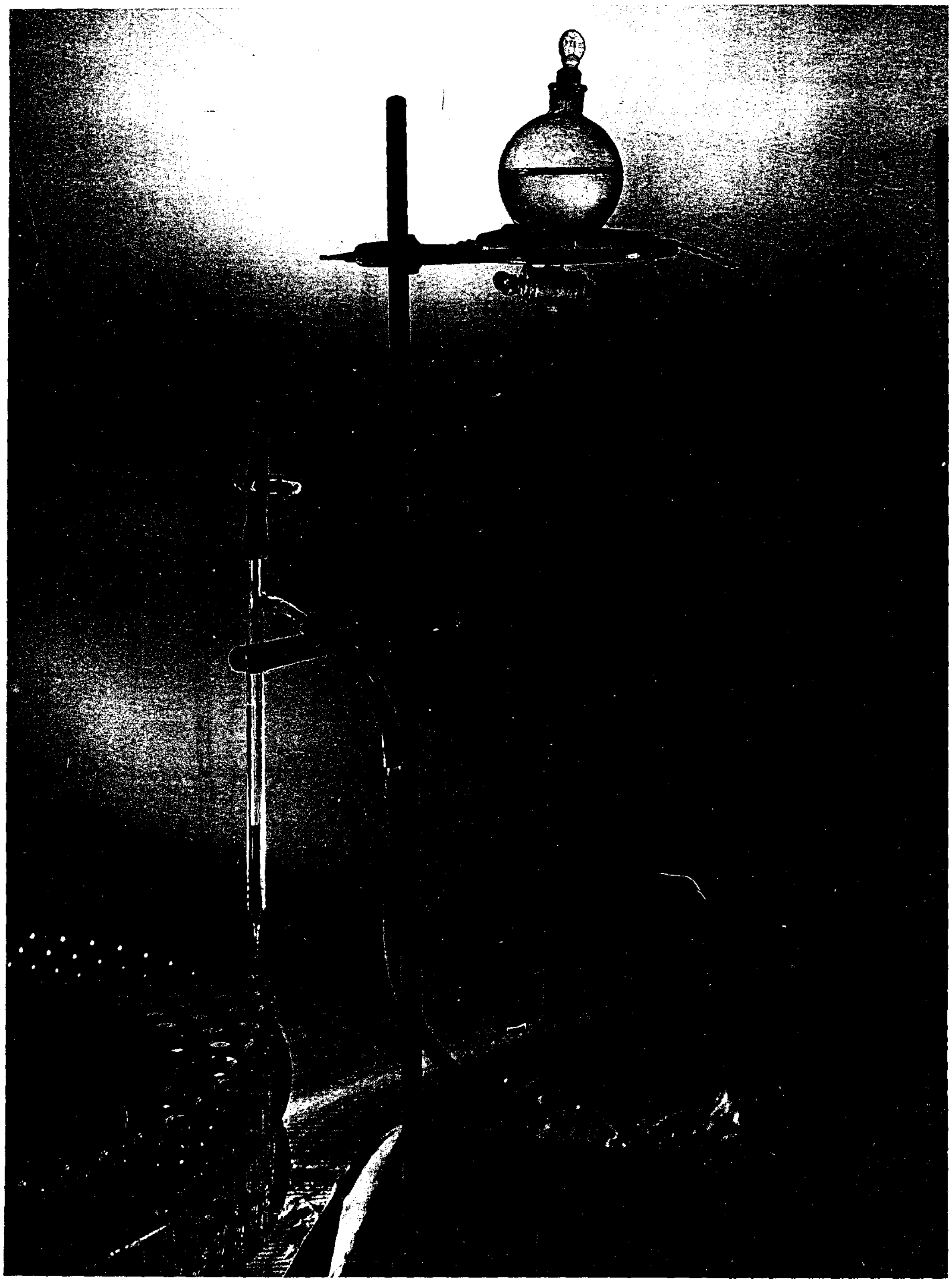

FIG. 4

red heat removed the citric acid. In some cases where extremely thin samples of the radioactivity were desirable for alpha-pulse analysis, berkelium was volatilized in a vacuum from a hot filament and collected on a platinum disc.

In those experiments directed toward the determination of the mass number of the berkelium isotope, a radiochemically pure element 97 fraction was obtained and after its decay the residual daughter activities were separated in another high temperature column employing Dowex-50 resin and ammonium citrate as the eluting agent as described above. Traces of Am^{241} and Cm^{242} were present and served to mark the positions of these elements in the fractions from the column. The thin plates made of these fractions were examined in the differential pulse analyzer and in the windowless proportional counter mentioned below.

Experimental Methods Used in Radioactivity Measurements

The thin deposits of the radiochemically pure element 97 fractions on platinum plates were examined in the differential alpha-particle pulse analyzer.[11] In this instrument individual pulses from an ionization chamber are sorted electronically and recorded on 48 fast mechanical registers in such a way as to separate the individual alpha-particle energies from a mixture of alpha-emitters. (A typical alpha-particle pulse analysis curve of the element 97 fraction is shown in Fig. 5.) In establishing values for the alpha-particle energies of the new isotope, direct comparison was made with pulse analyses of thin samples of isotopes, whose alpha-energies are well known, using the same instrumental conditions.

The thin deposits containing the element 97 fraction were also examined for any electron, x-ray, or gamma-ray radiations which might accompany decay

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[11] Ghiorso, Jaffey, Robinson, and Weissbourd, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 16.7 (McGraw-Hill Book Co., Inc., New York, 1949).

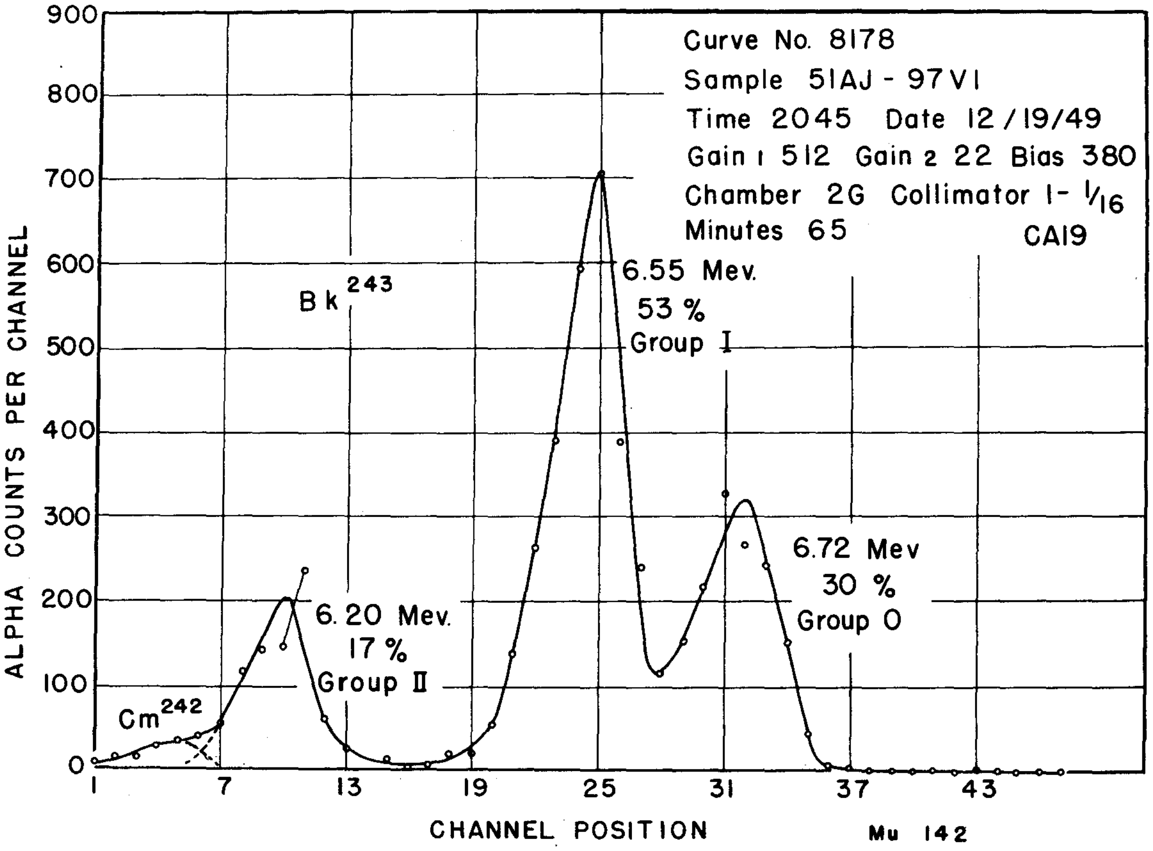

FIG. 5

Fig. 5 Typical alpha-particle pulse analysis curve of the 4.6-hour radioactivity obtained from the chemical separations of an element 97 fraction. The three alpha-particle groups, their energies and abundances are shown.

by electron capture. In some instances high efficiency was obtained by using a windowless proportional counter to detect Auger electrons. The samples obtained in the precipitation chemistry experiments (to be mentioned) were counted close to the thin window (3 mg/cm^2 mica) of a bell-jar-type Geiger counter filled with a mixture of 0.8 cm pressure of amyl acetate plus 11 cm pressure of xenon instead of the usual alcohol-argon mixture. The use of xenon enhances the efficiency for counting L x-rays. Hereafter in this paper this type of tube will be referred to as a xenon-filled Geiger tube. In the case of these relatively thick samples an aluminum absorber of thickness ~20 mg/cm^2 was used between the sample and counter window to reduce errors due to variable absorption of soft components as a function of differences in sample thickness. In some of the experiments samples were counted with various thicknesses of absorber (usually beryllium and beryllium together with lead) between the sample and the counter window in order to estimate energies and distinguish between electrons and electromagnetic radiations.

The L x-rays as counted in the xenon-filled Geiger counter were used as the basis for calculation of disintegration rates and total numbers of atoms. The L x-ray counting yield for the electron-capture isotope U^{231} had been determined previously by Crane, Ghiorso, and Perlman[12] using the same counter and conditions of measurement as were used by us. They compared the number of L x-ray counts of their U^{231} samples with the number of Pa^{231} daughter alpha-particles observed on complete decay. Defining counting yield as the number of L x-ray counts at ~10 percent geometry observed in a xenon-filled Geiger tube corrected to the number of counts at no absorber divided by the total number of electron-capture daughter atoms produced, Crane <u>et al</u>. obtain a counting yield of 0.0025. The same factor was used in our work to calculate the disintegration rate after making suitable corrections for the differences in absorption and in counting

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[12] Crane, Ghiorso, and Perlman, unpublished work.

efficiency in the counter used resulting from differences in energies of the x-rays of curium and protactinium. The use of this method tacitly assumes that the number of L x-rays emitted per disintegration is the same for the two isotopes U^{231} and Bk^{243}. There was some experimental justification for this as evidenced by the ratios of counting rates in the xenon-filled counter and in the windowless proportional counter. (These measurements made under as nearly identical conditions as possible gave ratios for the two isotopes which agreed within 5 percent.) Further justification was found in the observation that there are no significant numbers of soft gamma-rays of energies close to those of the L x-rays emitted in the decay of either isotope. This observation was made by pulse analysis of the pulses produced in a xenon gas-filled proportional counter using the same 48 channel instrument as was used in measuring alpha-particle energies. This method of x-ray energy determination is similar to one reported previously.[13] The energies of the L x-rays were established to be approximately those of curium and no extraneous soft gamma-rays were observed.

EXPERIMENTAL RESULTS

Results of Radioactivity Measurements

Applying the procedures described above to helium ion bombarded targets of Am^{241} and examining the radioactivity in the separated fractions expected to contain element 97 (if present), distinctive high energy alpha-radioactivity and radiations typical of the electron-capture process were revealed. All of the radioactivity decayed with a 4.6-hour half-life.

The results of a typical experiment in which alpha-particle energies and group abundances were measured by differential pulse analysis are shown in Fig. 5. The rate of decay of each energy group was measured by plotting the area under each peak versus the time of decay of the radioactivity. All three peaks were

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[13] Kirkwood, Pontecorvo, and Hanna, Phys. Rev. 74, 497 (1948).

observed to decay with a half-life of 4.6 ± 0.2 hours through a decay factor of more than 100. Furthermore, it was observed in examining berkelium fractions from separate bombardments that the ratio of the numbers of alpha-particles corresponding to the three different energy groups of the 4.6-hour activity remained constant regardless of the energy of the helium ions used for bombardment.

The radiations associated with the electron-capture decay were characterized in a qualitative manner by differential absorption in beryllium and lead absorbers using the xenon-filled Geiger counter previously mentioned. Present were electromagnetic quanta of energy 10 to 20 kev and harder electromagnetic quanta of energy greater than about 70 kev, some of which were probably K x-rays. No attempt was made to measure more energetic gamma-rays. Present also were conversion electrons of maximum energy of about 0.5 Mev, and the number of these electrons appeared to be about 5 percent of the total number of disintegrations based on the assumptions as to counting yield given in the previous section.

The half-life for the decay of the new berkelium isotope was also determined by observing the variation of its counting rate with time both in the windowless counter and in the xenon-filled Geiger counter. In the latter case three determinations, each with different absorbers placed between the sample and the counter window, were made. The absorbers used were 6.9 mg/cm^2 aluminum, 1.46 g/cm^2 beryllium and 1.46 g/cm^2 beryllium together with 93 mg/cm^2 lead above the beryllium, respectively. In all cases the counting rate was followed through a decay factor varying between 100 and 1000 giving a value for the half-life of 4.6 ± 0.2 hours.

The energies of the L x-rays associated with the decay of the new isotope were determined as mentioned previously. The data are best shown by reference to the typical pulse analysis curve of Fig. 6.

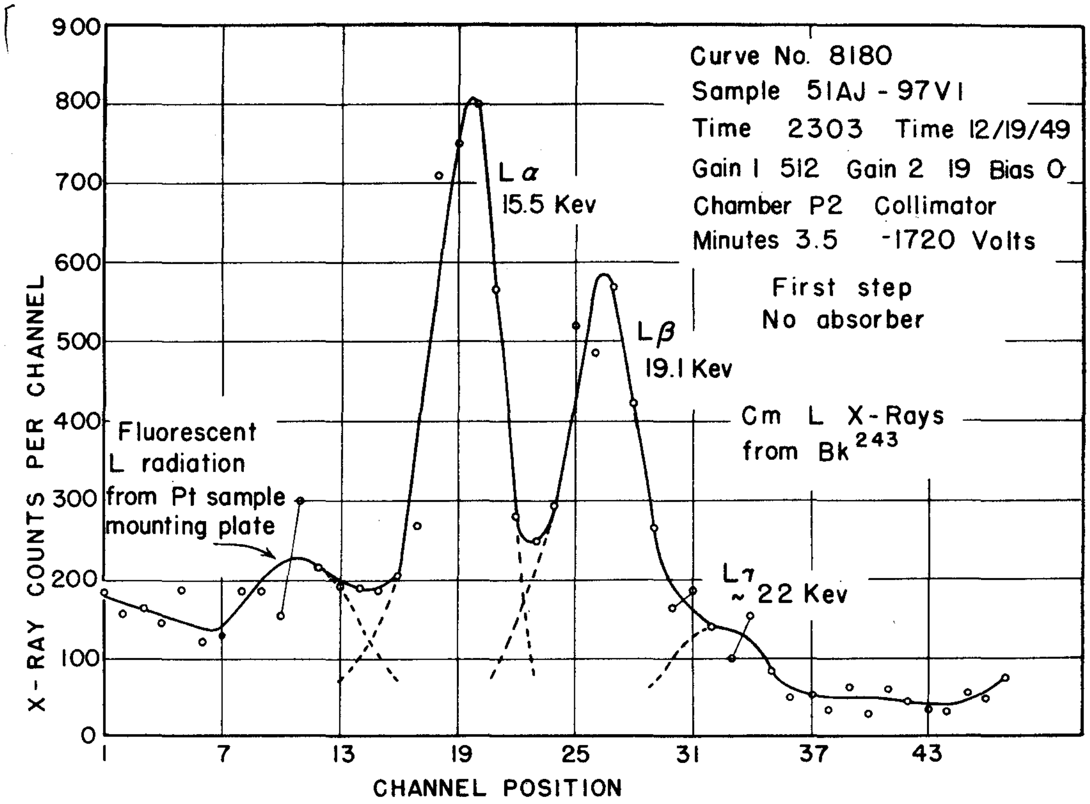

FIG. 6

MU 140

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Fig. 6. L x-ray pulse analysis of the electron-capture radiations of Bk^{243} using a xenon gas proportional counter connected to the differential pulse analyzer. The energies of these x-rays agree well with the values expected for curium.

Daughters of the Alpha-Particle and Electron-Capture Decay

Following the complete decay of the berkelium radioactivity, differential alpha-pulse analysis of the residual activity indicated the peaks shown in Fig. 7. The new alpha-particle group of 5.84 Mev energy was taken to be the orbital electron-capture daughter of berkelium. The other peaks represent Pu^{239} contamination introduced from plutonium left in the laboratory from other experimental work and small amounts of Cm^{242} and its daughter Pu^{238}, incompletely separated in the original column runs. In this connection it should be noted that all of the alpha-radioactivity in the sample amounts to only a few disintegrations per minute.

No decay of the unknown 5.84-Mev alpha-particle group occurred over a period of a few weeks. The chemical separations to be mentioned below showed that this new group belongs to a new curium isotope, and that it was produced by the electron-capture decay of the 4.6-hour berkelium activity. The amount of the new curium alpha-radioactivity observed, together with the initial electron-capture disintegration rate of the 4.6-hour activity in the same sample, made it possible to calculate an alpha-particle decay half-life of $\sim 10^2$ years for the curium isotope. In this calculation the method described in the section on experimental work was used in which the disintegration rate of the 4.6-hour activity was calculated from its L x-ray counting rate in the xenon-filled Geiger counter at the time the berkelium was first isolated from other radioactivities. From this value, the total number of curium atoms produced by the complete decay of the berkelium was calculated and this, together with the disintegration rate of the curium thus produced, were used to calculate the half-life.

The americium and curium daughters produced by the electron capture and alpha-particle decay of the new 4.6-hour activity were separated chemically using a Dowex-50 resin column according to the method previously described. This separation was made approximately 27 hours after the berkelium fraction had been isolated from other radioactivities. At this time all except about 2 percent of

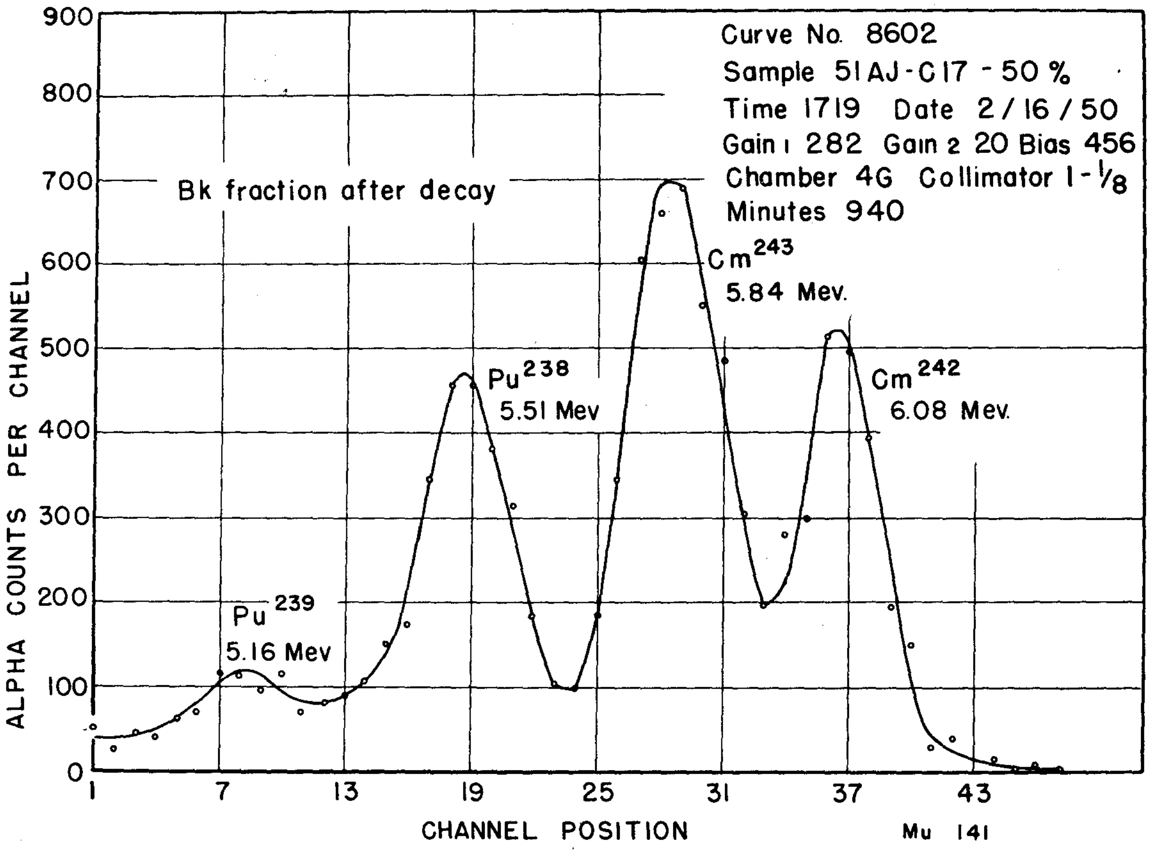

FIG. 7

Fig. 7. Alpha-pulse analysis of alpha-radioactivity remaining after complete decay of the 4.6-hour radioactivity. A new alpha-radioactivity of 5.84-Mev energy is observed which was proved by chemical separations to be a curium isotope of probable mass 243. The isotope Pu^{239} is present as low level contamination from other experimental work in the laboratory. The Cm^{242} and its daughter Pu^{238} are present as traces not completely removed in the chemical separations.

the berkelium had undergone decay so that the daughters were present as the result of essentially complete decay, but there was still enough berkelium present to indicate its position in the column elution sequence. Present also was a trace of Am^{241} to mark the position of americium isotopes. The elutriant fractions from the column showed the presence of the curium isotope with the alpha-particles of 5.84-Mev energy shown in Fig. 7, and a very small amount of an americium isotope of ~15 hours half-life as shown by counting Auger electrons in the windowless proportional counter (previously described).

It was only possible to follow the 15-hour activity through a very small decay factor (~2) so the probable error in half-life determination is about 40 percent. The background resulting from the presence of Am^{241} was approximately one-half the total counting rate. The amount of the 15-hour activity formed was very nearly the amount expected if it is due to electron-capturing Am^{239} produced[14] by the alpha-particle decay branching of Bk^{243} and if it is also assumed that the counting efficiencies in the windowless counter for these two isotopes are the same.

Branching Ratio and the Cross Section for Formation of Bk^{243}

The disintegration rates corresponding to measured fractions of the total berkelium produced in the bombardments were calculated from the L x-ray counting rates as previously described. The corresponding alpha-particle disintegration rates of the 4.6-hour activity allow a direct calculation of the alpha-decay to electron-capture decay ratio. The alpha-branching percentage was found to be ~0.1 percent. The corresponding partial half-life for alpha-particle emission is calculated directly as about 1 year.

The cross section for the production of the 4.6-hour activity in the bombardment of Am^{241} with 35-Mev helium ions is calculated as $\sim 10^{-26}$ cm^2. The corresponding

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[14] Street, Ghiorso, and Seaborg, Phys. Rev. (to be published).

cross section for the reaction at 30 Mev appears to be lower possibly by as much as a factor of two, although the latter value is less reliable. These calculations are based on the assumptions mentioned previously in regard to counting yields for the L x-rays.

Chemical Results - Ion Exchange Behavior

The behavior of the new 4.6-hour activity in the ion exchange separations used in its separation are highly significant for the assignment of the atomic number 97.

The results of the column separations involving ammonium citrate elution from a Dowex-50 resin column are best shown by the elution curve given in Fig. 8. This curve is a composite taken from several typical experiments. In some of the experiments the rare earth fission products were not removed until after the 4.6-hour activity had been separated from curium and residual americium; in such cases a direct comparison of the elution position of element 97 with the elution positions of some rare earth elements was obtained and these results are included in the composite curve of Fig. 8. The relative positions of the other rare earths were obtained from separate experiments done under as nearly identical conditions as possible. In all cases radioactive isotopes of the elements were present at tracer concentrations without added inactive isotopes. The activities were counted with a Geiger counter except for americium and curium whose alpha-particles were counted. The ordinate is given as counts per minute per drop; in some cases the counting rates are normalized to allow plotting on a scale suitable for comparison.

These results might be summarized thus: element 97 eluted in a position well ahead of curium as would be expected, and it was found between terbium and gadolinium in the rare earths.

A region of particular importance is illustrated in Fig. 9 which compares the elution positions of the group berkelium-curium-americium of the actinides with those of the homologous lanthanide group terbium-gadolinium-europium.

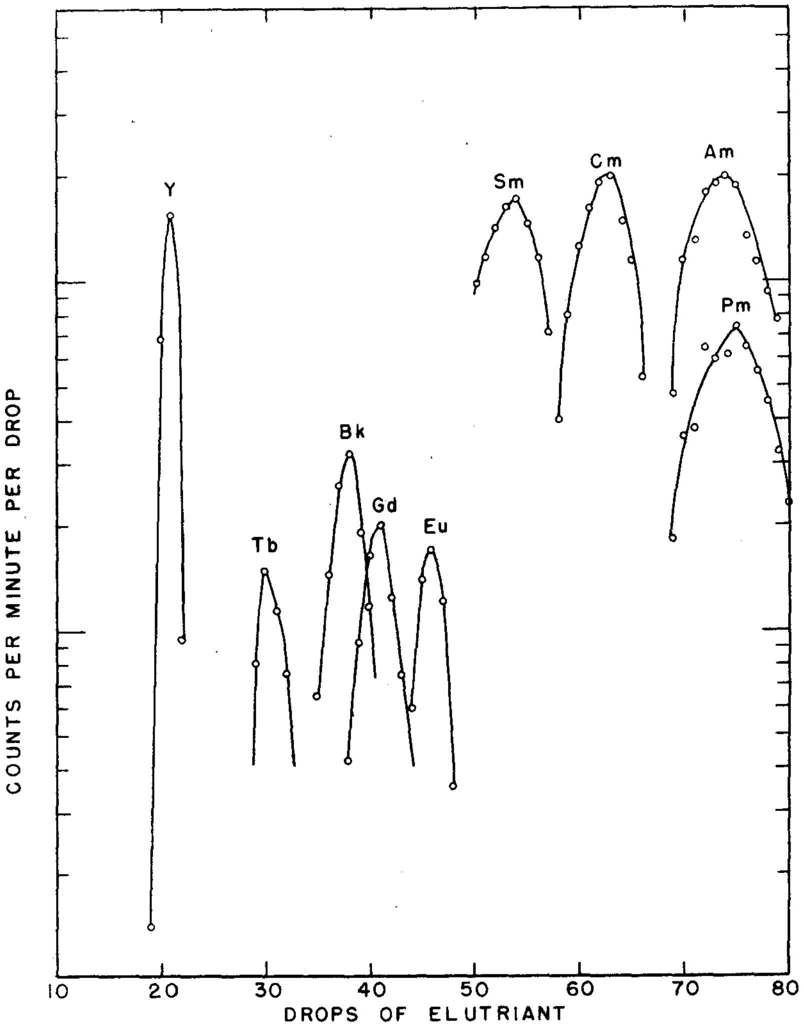

FIG. 8

Fig. 8. A composite curve showing the relative positions at which various actinide and lanthanide elements are eluted by an ammonium citrate solution from a column of Dowex-50 maintained at high temperature.

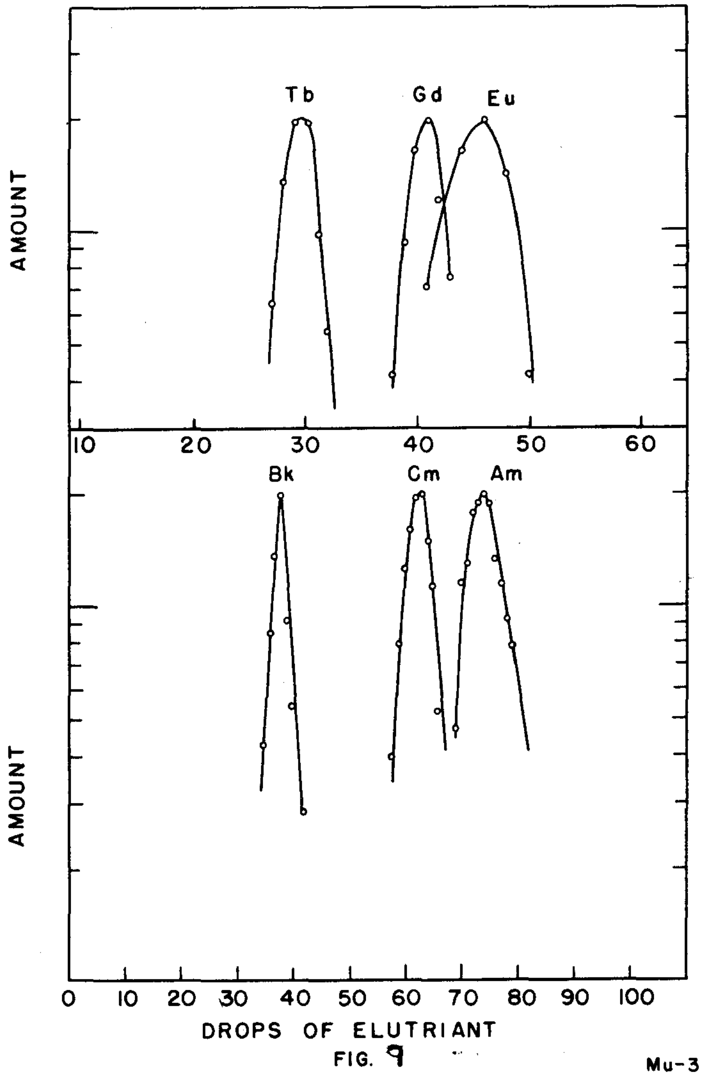

FIG. 9

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Fig. 9. Relative spacing of berkelium-curium-americium and their rare earth homologues, terbium-gadolinium-europium, in their elution from a high temperature Dowex-50 resin column with ammonium citrate solution.

Here the ordinates are normalized to show equal amounts. These results might also be summarized thus: the difference in rates of elution between berkelium and curium as compared with the difference between curium and americium is remarkably similar to the spacing terbium-gadolinium and gadolinium-europium.

With regard to the group separation of actinides from rare earths using the Dowex-50 resin column with 13M HCl, the new 4.6-hour activity was separated in the fractions containing curium and americium. These fractions were free of rare earth fission products which were removed from the column much more slowly because of the lesser extent of rare earth complexing with hydrochloric acid.

Chemical Results - Tracer Experiments

Using pure solutions of the 4.6-hour activity prepared by the ion exchange separations method a number of separate tracer experiments were performed to extend the knowledge of the chemical properties of the new element. Carriers such as lanthanum fluoride, lanthanum hydroxide, copper sulfide, zirconium phosphate, and ceric iodate were employed under conditions where the behavior of other actinide elements is well known. The oxidation-reduction properties of berkelium were studied with such agents as bromine, chlorine, dichromate ion, bromate ion, cerium (IV) ion, permanganate ion, and sodium bismuthate. In these experiments the distribution of the berkelium into the various fractions was determined by means of a Geiger counter. A complete report of these experiments is to be published elsewhere[15] but the salient results will be summarized here.

It was found that the 4.6-hour activity was not carried by zirconium phosphate unless powerful oxidizing agents such as bromate ion or sodium bismuthate were present; in the presence of these oxidizing agents it was well carried. It was well carried by the carriers lanthanum fluoride or lanthanum hydroxide in solutions ranging from strongly reducing to strongly oxidizing.

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[15] Thompson, Cunningham, and Seaborg, J. Am. Chem. Soc. (in press), May, 1950.

In the case of lanthanum hydroxide, excellent carrying was obtained regardless of whether potassium hydroxide or ammonium hydroxide was used for precipitation of the carrier. In the absence of oxidizing agents, the 4.6-hour radioactivity was not carried by the insoluble sulfides of copper and bismuth precipitated in 0.3M HCl; and in strong hydrochloric acid, it was not adsorbed by the anion exchange resin Dowex A-1. By means of the use of various oxidizing agents including mixtures of cerium (III) and cerium (IV), the 4.6-hour activity was found to have behavior so near to that of cerium as indicated by carrying or non-carrying with zirconium phosphate and ceric iodate that the oxidation potential for the couple $\text{Bk (III)} \longrightarrow \text{Bk (IV)} + e^-$ must be about -1.6 volts on the scale where the hydrogen-hydrogen ion potential is zero.[16] These results may be summarized thus: element 97 has properties closely resembling those of cerium, particularly with regard to its oxidation potential. However, differences between berkelium and cerium were observed in the properties of the tripositive oxidation state where berkelium is more like terbium (III), as shown by resin column separations. With 13M HCl, of course, relatively large differences between berkelium (III) and all rare earths were observed.

DISCUSSION OF RESULTS

The experiments and results which have been given provide the evidence for the discovery of an isotope of element 97. That the 4.6-hour activity observed in the experiments is beyond reasonable doubt an isotope of element 97 is proved by the following essentially independent means:

(1) Its separation in the "eka-terbium" position expected for element 97 in elutriant fractions from the Dowex-50 resin column with ammonium citrate as the eluting agent. The relative spacing between berkelium and its actinide neighbors is remarkably similar to the relative spacings between the homologous lanthanides.

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[16] W. M. Latimer, Oxidation Potentials (Prentice Hall, Inc., New York, 1938).

(2) Its behavior with various carriers and oxidizing agents which showed it to be similar to cerium with regard to its oxidation potential. The cerium and all rare earth fission products were separated from it by means of the Dowex-50 resin column employing hydrochloric acid as the eluting agent.

(3) Its radioactive properties, particularly the high alpha-particle energies. This may be illustrated by referring to Figs. 6, 7, 8, and 9 of reference 4 which show the alpha-half-life vs. energy relationships of various nuclides as a function of atomic number. That the atomic number is clearly greater than 94 is also proved by measurement of the energy spectrum of the L x-rays in the xenon proportional counter connected to the pulse analyzer. It may be noted there are no known plutonium, americium, or curium isotopes of 4.6-hour half-life.

(4) The identification of curium and americium daughters which are produced by electron capture and alpha-particle decay.

The best evidence in regard to the mass assignment is in the growth of the americium daughter activity of half-life ~15 hours which must have been produced by the alpha-particle decay of the 4.6-hour activity. The small amount of this ~15-hour activity observed made it difficult to determine a precise value of the half-life or to characterize the radiations. However, the only known americium isotope of similar half-life characteristics is the 12-hour electron-capture isotope Am^{239} whose assignment is practically certain.[14] The activities were sufficiently similar and the amount of the 15-hour activity sufficiently near expectations as to make the identification probable. Therefore, the mass number of the 4.6-hour berkelium activity is probably 243.

The growth of the curium isotope which emits alpha-particles of about 5.84-Mev energy also suggests the assignment to mass 243 for the following reasons. Other experiments performed in this laboratory have indicated that Cm^{244} emits alpha-particles of slightly different energy, namely, 5.79 Mev and that its alpha-half-life is of the order of 10 years.[17] The amount of curium daughter alpha-radioactivity which was formed by the electron-capture decay of the berkelium isotope indicated that the alpha-decay half-life of the new heavy curium isotope was of the order of 10^2 years. This energy and half-life would agree best with the alpha-decay systematics[4] if assigned to Cm^{243}. In this connection it should be pointed out that 30-Mev helium ions used in the lowest energy bombardment of the americium are below the threshold for the $(\alpha,4n)$ reaction in this region so that berkelium isotopes of mass number less than 242 should not have been produced. The observed cross section ($\sim 10^{-26}$ cm^2) is of the same order of magnitude as cross sections for the $(\alpha,2n)$ reaction with helium ions of 30-to 35-Mev energy in the production of other heavy isotopes.

When the three alpha-particle groups of the 4.6-hour activity were first observed, the possibility was indicated that more than one isotope of element 97 might be present. This possibility was eliminated as follows: All three groups decayed with 4.6-hour half-life as did the electron-capture radiations. There was no difference in the ratios of the three groups when the energies of the helium ions used in the bombardments were varied. If another isotope has been present in significant amounts, its daughters would have been detected.

It is interesting to consider the explanation of the three groups of alpha-particles. Reference to the half-life vs. energy relationships for the odd atomic number nuclides as given in Fig. 8 of reference 4 shows that an alpha-decay half-life of the order of a day or less might be expected for an isotope of element 97 with an unforbidden transition having a maximum alpha-particle energy of 6.72 Mev. Therefore, alpha-particle decay in the isotope 97^{243} is highly forbidden, perhaps by a factor of 10^2 or 10^3. Since the transition between ground states is highly forbidden, the transition to excited states of the product nucleus

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[17] Street, Ghiorso, and Thompson, unpublished work.

becomes probable even though the total difference in energy involved is less, so it is reasonable to have low energy alpha-groups of intensity comparable to the ground state transition. This is not unreasonable for a nucleus with an odd nucleon (proton) like Bk^{243}.

It is also interesting to consider the relationship between energy and the half-life for electron capture. The disintegration energy of Bk^{243} may be calculated by means of the closed cycles and used to estimate a half-life for electron capture by the method of Thompson.[5] The disintegration energy so obtained gives a half-life of considerably less than one hour if applied to the curve[5] which includes most of the data. The new isotope appears to represent a case whose electron-capture decay is more forbidden than most of the other heavy odd-even type nuclei. This situation is, of course, fortunate insofar as the identification of the new element is concerned. If the isotope Bk^{243} had not been forbidden with respect to decay by electron capture, the identification of the new element might have been delayed until even more rapid chemical separations and techniques could be developed. The other isotopes of berkelium formed in the present bombardments are presumably all shorter-lived than Bk^{243}.

SUMMARY

An isotope of element 97 (berkelium, symbol Bk) has been produced and identified. This isotope probably has the mass number 243 as produced in the reaction $Am^{241}(\alpha,2n)Bk^{243}$. It decays predominantly by electron capture with a half-life of 4.6 ± 0.2 hours and exhibits ~0.1 percent alpha-particle decay branching. The alpha-particles are of three groups, the maximum energy being 6.72 Mev (30 percent). The other two energy groups are 6.55 Mev (53 percent) and 6.20 Mev (17 percent). The bombardments were made with 30- to 35-Mev helium ions in the Berkeley Crocker Laboratory 60-inch cyclotron. The chemical separations were made using a combination of precipitation methods and high temperature ion

exchange columns with Dowex-50 resins. The growth of a curium isotope decaying by the emission of alpha-particles of energy 5.84 Mev was observed in a radiochemically pure berkelium fraction. This curium isotope is probably Cm^{243} produced by the electron-capture decay of Bk^{243}. Chemical separations on the decay products of the Bk^{243} also revealed an americium isotope of ~15-hour half-life, which appears to be identical within the limits of error of the experiment with the known 12-hour electron-capturing Am^{239}. The cross section for the formation of Bk^{243} by the $(\alpha,2n)$ reaction is $\sim 10^{-26}$ cm^2. The chemical properties of the berkelium are typical of those of the actinide elements. Its tripositive oxidation state bears the same relationship to curium as does terbium to gadolinium as shown by the separations on ion exchange resin columns. The analogy between these two groups of elements is apparent, indicating the same kind of break in ionic radius at the point of half-filling of the 5f electron shell (curium) for the actinide elements as has been known to exist for the analogous point of half-filling of the 4f electron shell (gadolinium) for the lanthanide elements. The oxidation potential for the (III) $\longrightarrow$ (IV) couple of berkelium is close to that of the corresponding couple for cerium (~-1.6 volts).

NAME

It is suggested that element 97 be given the name berkelium (symbol Bk) after the city of Berkeley in a manner similar to that used in naming its chemical homologue terbium (atomic number 65) whose name was derived from the town of Ytterby, Sweden, where the rare earth minerals were first found.

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