the rate of exchange of an individual C–H bond so that all the hydrogens will be exchanged before these alkyl groups can desorb as alkanes. To differentiate between these two points of view one will have to study the dependence of the exchange on the pressure of hydrogen and to study the exchange between a fully protiated and a fully deuterated hydrocarbon. It was further shown that when C–C bonds are broken in propane and the butanes, they are all broken since the degradation product consists solely of methane.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA]

First Isolation of Curium

BY L. B. WERNER* AND I. PERLMAN

The first isolation of curium in microgram quantity from neutron-irradiated americium is described. The americium and curium were separated by the use of an ion exchange resin and the curium further purified and isolated as the fluoride and hydroxide. The absorption spectrum of curium(III) was measured and attempts were made to determine the specific activity of a sample of curium oxide weighing about 40 micrograms.

Introduction

The discovery of element number 96, curium, was accomplished by the identification of Cm^{242} following preparation of this nuclide by cyclotron bombardment of Pu^{239} with helium ions.[1] Cm^{242} is an alpha emitter having a 162 day half-life.[2] It may also be prepared by neutron irradiation of Am^{241} according to the reactions[1]

$$Am^{241}(n,\gamma)Am^{242}$$

$$Am^{242} \xrightarrow[18\text{ hr.}]{\beta^-} Cm^{242}$$

The prolonged neutron irradiation of plutonium led to the production of milligram amounts[3] of Am^{241} and its isolation.[4] Still further neutron irradiation of the americium has made it possible to prepare microgram quantities of Cm^{242}. Microgram amounts of material have been found sufficient to prepare pure compounds of other transuranium elements and to investigate the properties of their solutions at ordinary concentrations (10^{-3} to 10^{-1} M) on the "ultramicro" scale of chemical operations[5] and extensive use of such techniques was made in the present study.

The chemistry of curium as determined on the tracer scale has indicated that only the tripositive oxidation state exists in aqueous solution.[6] According to the actinide concept of the structure of the heaviest elements[7] curium is the seventh member of a series in which the f-orbitals lie at progressively lower levels. Because a half-filled shell, in this case with $5f^7$ configuration, might be expected to have added stability, the predominance of Cm(III) which is thought to have this configuration would be expected over other oxidation states. In this respect curium would be analogous to gadolinium in the rare earth series.

At the time this problem was undertaken americium was not known to have an oxidation state other than the trivalent state. (As part of the study it was found possible to oxidize americium to Am(V) in alkaline solution[8] and others[9] showed it possible to produce Am(VI) in acid solution.) Since there seemed little likelihood that the oxidation of curium could be changed as an aid in its separation from americium, the problem of isolating curium resolved itself into one of separating two tripositive ions similar to two adjacent rare earths. In addition, small amounts of various impurities existed in the americium which were comparable in weight to the curium itself. Of still another nature was the appearance of Pu^{238} which grows from the alpha decay of Cm^{242} at the rate of nearly 0.5% per day.

Separations of rare earth elements have been successfully carried out by the use of ion exchange methods.[10] Such methods offer much in simplicity of operation and for quantitative recovery of the components and formed the basis for the curium–americium separation to be described.[11] Those impurities not removed by the specific curium–americium separation could be separated by precipitation steps carried out from very small volumes of solution.

To check on the purity of the isolated curium, spectrographic analysis was made and in addition a specific activity determination of curium oxide was attempted. This latter determination consisted of weighing a sample of curium oxide which weight could be compared with the amount of curium known to be in the sample from radiometric assay. Among other properties determined from

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* Now at the Naval Radiological Laboratory, San Francisco, California.

(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, N. Y., 1949.

(2) G. C. Hanna, B. G. Harvey and N. Moss, *Phys. Rev.*, **78**, 617 (1950).

(3) A. Ghiorso, R. A. James, L. O. Morgan and G. T. Seaborg, *ibid.*, **78**, 472 (1950).

(4) B. B. Cunningham, unpublished.

(5) B. B. Cunningham and L. B. Werner, THIS JOURNAL, **71**, 1521 (1949).

(6) S. G. Thompson, L. O. Morgan, R. A. James and I. Perlman, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 19.1, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(7) G. T. Seaborg, *Nucleonics*, **5**, no. 5, 16 (1949).

(8) L. B. Werner and I. Perlman, THIS JOURNAL, **73**, 495 (1951).

(9) L. B. Asprey, S. E. Stephanou and R. A. Penneman, *ibid.*, **72**, 1425 (1950).

(10) D. H. Harris and E. R. Tompkins, *ibid.*, **69**, 2792 (1947).

(11) B. B. Cunningham, E. R. Tompkins and L. B. Asprey (unpublished April, 1947) first demonstrated the usefulness of the cation exchange column method for separating americium and curium, using Dowex-50 and room temperature elutions with 0.25 M ammonium citrate plus citric acid at pH of 3.05.

the isolated curium was the absorption spectrum of Cm(III) in aqueous solution.

Experimental

A sample of 4.48 mg. of americium as the oxide was irradiated under a high flux of slow neutrons for about one year. Nearly 3.5% of the sample consisted of impurities, largely lanthanum with smaller amounts of yttrium, calcium and magnesium. The sample was dissolved from its platinum container by addition of dilute nitric acid. Preliminary chemical operations carried out by other members of the laboratory were designed to remove other nuclides of interest.[12] The sample was received as a dilute hydrochloric acid solution containing most of the americium and 150 μg. of curium.

Separation of americium from curium was accomplished by use of a 50-cm., 8-mm. diameter column packed with 200–300 mesh colloidal agglomerates of Dowex-50 ion-exchange resin.[13]

Americium and curium were first adsorbed from aqueous solution at *p*H 1 with *ca.* 0.2 ml. of the resin. Active resin was layered at the top of the 50-cm. column and a 0.25 *M* citric acid solution at *p*H 3.05 was passed through the column at a flow-rate of 0.4 ml./cm.^{2}/min. A total of 142 samples of eluant each having a volume of 2.5–3 ml. were collected and analyzed for alpha activity. The distribution of radioactivity is shown in Fig. 1. Alpha particle energy analysis using a differential pulse analyzer[14] was performed on samples with appreciable radioactivity and these showed the amounts of americium and curium in the various samples. Those containing curium essentially free of americium were combined. Those containing americium with significant amounts of curium were combined and again subjected to the ion exchange separation. Approximately 115 micrograms of curium essentially free of americium were obtained in 50 ml. of solution. Nearly 5% of the sample had been lost by radioactive decay at this point.

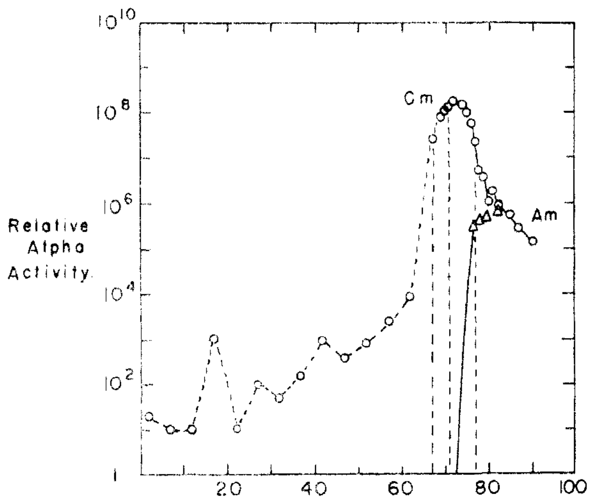

Fig. 1.—Elution curve of americum and curium (second column).

Concentration of the sample was achieved by readsorption at *p*H 1 using several small portions of ion exchange resin, from which curium was subsequently eluted batchwise with 0.25 *M* citrate solution at *p*H 5. Following evaporation and decomposition of the citrate solution with nitric and sulfuric acids, two precipitations of curium hydroxide from ammoniacal solution served to remove ammonia soluble impurities. The slightly yellow gelatinous precipitates of curium hydroxide, which showed an apparent solubility of *ca.* 10 μg./ml., bubbled vigorously due to decomposition of water by the alpha radiation. After dissolution of the hydroxide precipitate with hydrochloric acid, 100 μl. of 0.5 *M* hydrochloric acid solution containing 89 μg. of curium was placed in a quartz microabsorption cell and absorption spectrum measured from 3200 to 11,000 Å. using a Beckman model DU spectrophotometer. It was found necessary to remove the cell carriage and tap it sharply at frequent intervals to dislodge gas bubbles which formed continuously. The absorption curve is shown in Fig. 2. The small peak at 5040 Å. was assumed to be due to Am(III) which shows strong absorption at this wave length. From the height of this peak the maximum amount of americium present was calculated to be *ca.* 0.5% of the weight of the curium. The curium itself apparently shows no absorption in the visible spectrum but absorbs heavily in the ultraviolet region.

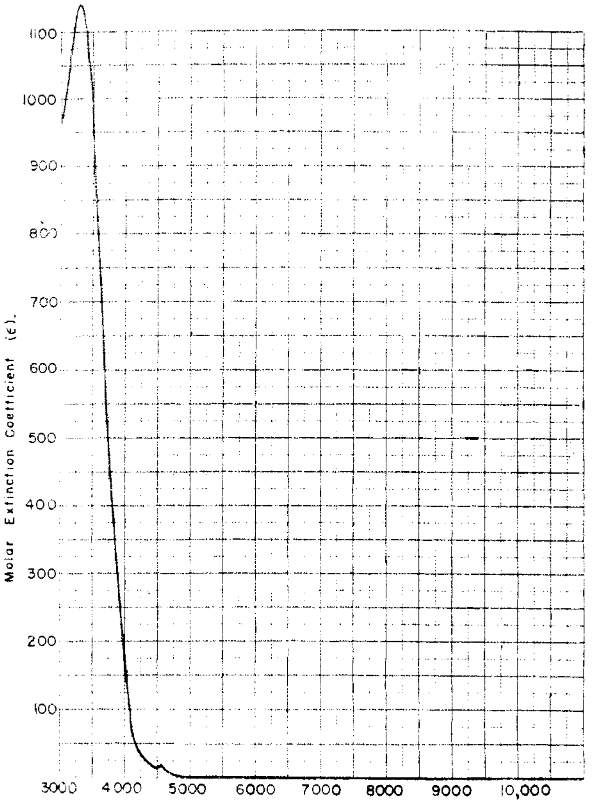

Fig. 2.—Absorption spectrum of Cm(III) in 0.5 *M* HCl.

Further purification of the sample was carried out as follows: a dilute nitric acid solution of curium was made *ca.* 0.1 *M* in argentic ion. This served to oxidize the Pu^{238} daughter of Cm^{242} to a fluoride soluble state. Curium fluoride was precipitated by making the solution 3 *M* in hydrofluoric acid; the apparent solubility was found to be *ca.* 20 μg./ml. By treating the precipitate with several portions of concentrated ammonia solution, curium fluoride was converted to curium hydroxide, which was subsequently dissolved in 0.1 *M* hydrochloric acid. At this point approximately 50 μg. of curium remained. Two 2% portions of the sample submitted for spectrographic analysis showed no impurities other than lead in an amount equal to *ca.* 10% of the weight of the curium. Saturation of the curium solution with hydrogen sulfide caused a black precipitate which was subsequently removed by centrifugation. Curium hydroxide was precipitated, washed, and dissolved in dilute nitric acid. Nearly 10% of the sample was submitted for a complete spectrographic analysis.[15] The only impurity

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(12) The americium used in this study was made available by Drs. B. B. Cunningham and S. G. Thompson, who also conducted the initial separations.

(13) Provided by the Dow Chemical Company, Midland, Michigan.

(14) A. Ghiorso, A. H. Jaffey, H. P. Robinson and B. B. Weissbourd, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 16.8, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(15) In performing this analysis Mr. John Conway observed the following strong lines of the curium emission spectrum: 3427.0, 3472.4, 3552.9, 3904.8, 4207.1 Å. More complete measurement of the emission spectrum has since then been made.[16]

(16) J. G. Conway, M. F. Moore and W. W. T. Crane, THIS JOURNAL, 73, 1308 (1951).

detected was lead in an amount 1% of the weight of curium present.

Determination of the specific activity of the curium preparation was carried out as follows. The oxide of curium was prepared by igniting curium nitrate in a special platinum capsule. Detail of the construction of the capsule is shown in Fig. 3. Since the oxide was to be weighed on a quartz beam microbalance, it was necessary to use containers whose weight was below the load capacity of the balance. In order to confine the highly active sample during the weighing operations, the capsule was crimped shut after ignition and enclosed within a similar capsule of slightly larger diameter. Manipulation of the loaded capsule was readily accomplished by means of a "vacuum pickup," a $^1/_4$-inch diameter brass tube fitted at one end with a short piece of fine platinum capillary tubing and connected to a vacuum. By opening and closing the vacuum connection the capsule could be alternately held at the capillary end of the pickup and dropped into position. Remote handling of the sample was thereby facilitated with little danger of damage to the fragile containers.

Calibration of the quartz balance was achieved as follows. Nineteen aluminum strips approximately 0.5 × 5 mm. in size were cut from 1 mil aluminum foil and weighed individually on the quartz balance; the sum of the weights produced a displacement corresponding to 15,436 divisions. Using an Ainsworth microbalance to determine the weight of the combined strips, an average result of 2.655 ± 0.003 mg. was found for two weighings. The calibration factor of the balance was therefore $2.655/15{,}436 \times 1000 = 0.1720$ μg./div.

By use of a micropipet a curium nitrate solution was placed in the capsule and carefully evaporated to dryness. The capsule was held in a short piece of quartz tubing surrounded by a platinum resistance heating coil. The temperature of the coil was gradually increased until the capsule reached bright red heat. After one-half hour at this temperature the sample was cooled and immediately placed on the balance.

Following the initial reading, a gradual increase in the weight of the entire sample was observed over a period of ten days. An examination of various factors led to the conclusion that the increase could best be accounted for by radiation-induced oxidation of the platinum containers. By extrapolation back to the time of ignition the weight of the oxide sample was found to be 45.2 μg. Nearly two weeks after the initial heating the sample was again ignited and weighed. The capsules were carefully opened. Microscopic examination showed a brown amorphous solid lining the wall and bottom of the inner capsule. This material was dissolved readily by several additions of concentrated nitric acid. The solution of curium nitrate was diluted to exactly 1 ml. and a 1.075-μl. aliquot was removed and counted in a low-geometry alpha particle chamber. It was found that the activity of the total sample was 2.26×10^{11} disintegrations per minute, corresponding to 30.7 μg. of pure Cm^{242} at the time the alpha analysis was made. The empty platinum containers were checked for alpha activity and found to be clean. They were then dried and reweighed. A second value for the weight of the oxide thus was obtained which was 41.6 μg. Considering the known constituents of the sample and the amount of pure Cm^{242} found to be present by alpha analysis, the composition of the sample at the time of the first ignition was found to be

Cm_2O_3	36.2 μg.
PuO_2	2.1 μg.
Am_2O_3	1.9 μg.
PbO	0.4 μg.
Total	40.6 μg.

This left unaccounted for $45.2 - 40.6 = 4.6$ μg. or *ca.* 10% of the sample which was presumed to be previously undetected impurities. At the time of the second ignition the composition of the sample was calculated to be

Cm_2O_3	33.8 μg.
PuO_2	4.7 μg.
Am_2O_3	1.9 μg.
PbO	0.4 μg.
Total	40.8 μg.

This left $41.6 - 40.8 = 0.8$ μg. or *ca.* 2% of the sample unaccounted for. The discrepancy between the two results is outside the error which may be expected either of alpha assay or of weighing on the quartz microbalance; it was presumed to result from the uncontrolled apparent weight change of the sample during the weighing operation.

We have concluded that the curium oxide preparation was of the order of 85–93% pure.[17]

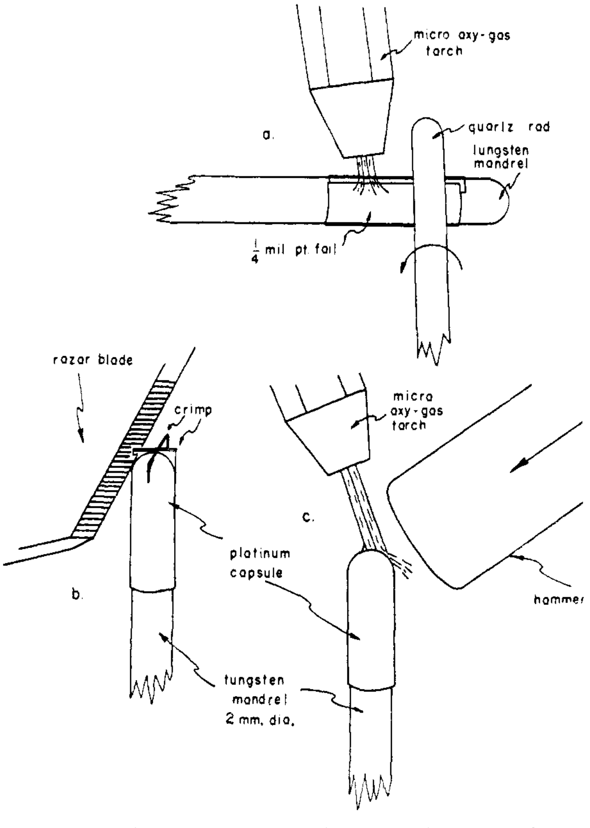

Fig. 3.—Construction of platinum weighing capsule.

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[17] PuO_2 present was not considered an impurity.