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CHEMICAL PROPERTIES OF BERKELIUM

Stanley G. Thompson and Glenn T. Seaborg

February 24, 1950

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CHEMICAL PROPERTIES OF BERKELIUM

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February 24, 1950

The recent production by Thompson, Ghiorso, and Seaborg[1] of a radioactive isotope of berkelium (atomic number 97) makes it possible to investigate the chemical properties of this transuranium element by means of the tracer technique. This isotope has been prepared through the bombardment of Am^{241} with about 35 Mev helium ions in the 60-inch cyclotron of the Crocker Laboratory and is believed to have the mass number 243, or possibly 244. This Bk^{243} has a half-life of 4.6 hours and decays by electron capture with about 0.1 percent branching decay by alpha-particle emission.

In the present tracer chemical experiments, the radiations accompanying the electron capture process were used as a means of detection and were counted in two ways. Where the sample deposits on the platinum plates were essentially weightless, as was the case following the evaporation and ignition of the elutriant solutions in the column adsorption experiments, a high efficiency was obtained by using a windowless proportional counter to count the Auger electrons. The thicker samples from the precipitation experiments in which carrier materials were used were counted close to the thin window (3 mg/cm^2 mica) of a bell type Geiger counter filled with 10 cm. xenon to enhance the efficiency for counting the x-rays. An aluminum absorber of thickness about 20 mg/cm^2 was used between the sample and counter window to reduce errors due to variable absorption of soft components caused by small differences in sample thickness.

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(1) S. G. Thompson, A. Ghiorso, and G. T. Seaborg, Phys. Rev., 77, in press.

The tracer Bk^{243} was isolated by a combination of chemical procedures including the use of a cation exchange resin (Dowex 50). Following the bombardment, most of the americium was separated from the curium (largely Cm^{242}, formed in the bombardment), berkelium, and the rare earth fission products by oxidizing the americium to above the III and IV oxidation states. Following this the precipitation of insoluble fluoride using some carrier such as lanthanum separated a fraction containing unoxidized radioactive americium, curium, berkelium, yttrium, and the rare earth fission products from the remainder of the fission products. The three heavy elements, americium, curium, and berkelium, were then separated from the others by adsorbing the dissolved mixture on the resin and selectively eluting[2] them with 13<u>M</u> HCl which forms complex ions with the actinide elements but not with the lanthanide elements.

The berkelium, curium, and americium were separated from each other through the use of the Dowex 50 ion exchange resin under the following conditions. The mixture was adsorbed on a small amount of the resin and placed on top of a column 2 mm. in diameter and 20 cm. long, packed with the ammonium salt of the resin in fine spherical form. The eluting agent was ammonium citrate (buffered with citric acid to pH 3.5 - total citrate concentration 0.25<u>M</u>). In order to decrease the time of separation, the elution was carried out at an elevated temperature of about 87°C. The flow rate of the eluting agent was held at one drop (~ 0.030 cm^3) about every two minutes.

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(2) K. Street, Jr., unpublished work.

Figure 1 shows the plot of the elution peaks of berkelium, curium, and americium. Similar data are also included for yttrium and the rare earths promethium, samarium, europium, gadolinium and terbium for purposes of comparison. As it was more convenient for our purposes first to separate the actinide elements from lighter elements, Figure 1 showing the citrate elution curves is a composite of several separate experiments carried out under as nearly identical conditions as possible. The radioactive isotopes of these elements were present at tracer concentrations without added inactive isotopes. The ordinate is given as counts per minute per drop, where the counting was done with a Geiger counter, for all except americium and curium whose alpha-particles were counted. The data are given in this direct manner since in tracer experiments of this type the relative amounts are unimportant and no purpose is served by calculating the number of atoms on an absolute basis through the use of the half-lives and counting efficiencies of the isotopes concerned.

Since a more careful comparison of the two groups, berkelium-curium-americium and terbium-gadolinium-europium, is of primary interest, the data for these elements are plotted in Figure 2 in a manner which facilitates this comparison. Here the ordinates are normalized for convenience to show equal amounts. A remarkable 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). It may be seen also that the difference in rates of elution is greater between neighboring actinides than it is for the corresponding lanthanides.

Fig. 1.-- Elution of Bk, Cm, Am, Y, Tb, Gd, Eu, Sm, Pm from Dowex-50 with ammonium citrate at 87°C.

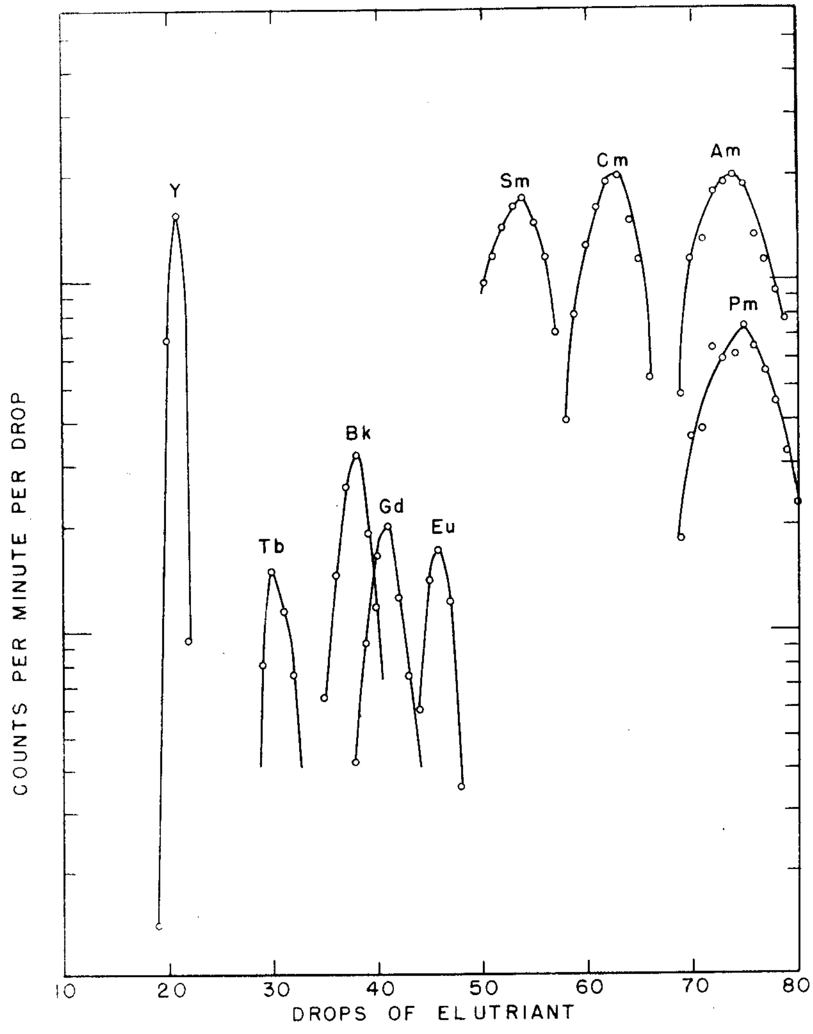

FIG. 1

Mu-31

14 593-1

Fig. 2.-- Comparison of elution of Bk, Cm, Am with their homologues Tb, Gd, Eu.

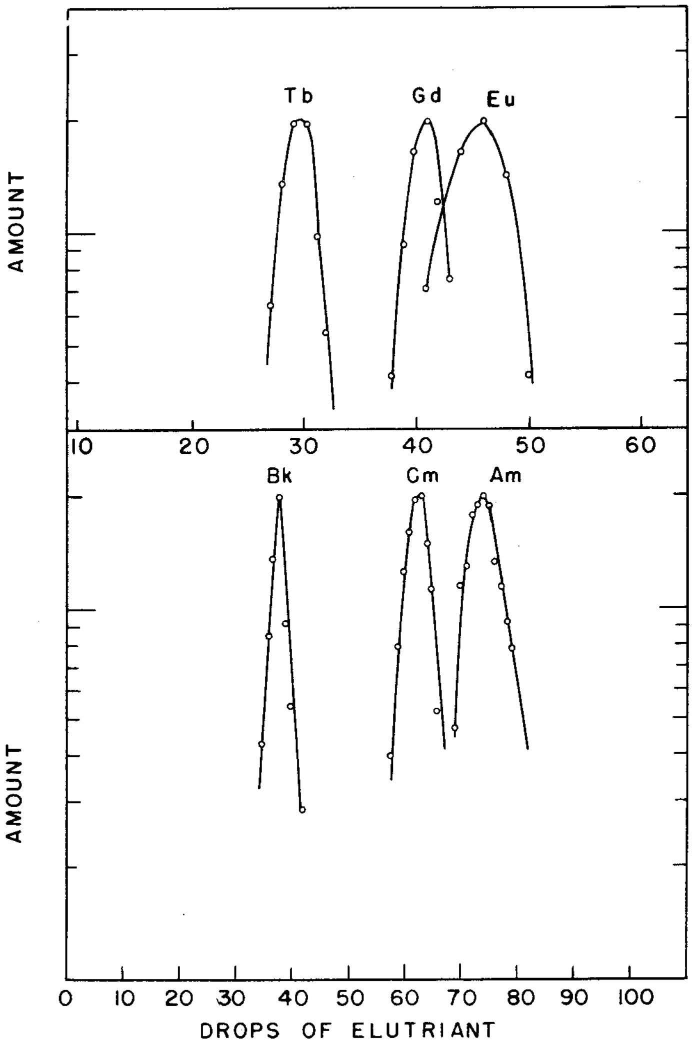

FIG. 2

Mu-32 14592-1

In view of the anticipated similarity of berkelium to its rare earth homologue terbium, attempts were made to oxidize the predominantly tripositive berkelium in aqueous solution to the IV oxidation state. It is known that terbium, the first element beyond the middle of the lanthanum group, can be oxidized to the IV state as solid TbO_2, but that this oxidation is not possible in aqueous solution. It was predicted[3] that element 97 should have a IV as well as a III oxidation state and this should be easier to reach than is the case for terbium. In fact it seemed quite likely that it should be possible to effect this oxidation in aqueous solution, and this has proved to be the case.

Table I shows the results of a series of carrying experiments in which solutions containing Bk^{243} tracer were treated with oxidizing agents of various strengths. Carrying with zirconium phosphate or cerium (IV) iodate was used as the test for oxidation, it being assumed that Bk(IV) would be carried and Bk(III) not carried by these precipitates. After the separation of the precipitate, a precipitation of lanthanum fluoride was made from the supernatant in order to check the amount remaining there. It has been shown in many experiments that lanthanum fluoride carries Bk(III) fluoride quantitatively and, in fact, all indications point to similar behavior of Bk(III) in other chemical properties to that of the tripositive actinide and lanthanide elements. In the zirconium phosphate or cerium(IV) iodate experiments, carrying of some 90% of the berkelium is considered to represent essentially complete oxidation to the IV state, while carrying of some 5% is considered to represent no oxidation on the basis of analogy with the behavior of other actinide elements in tracer experiments.

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(3) G. T. Seaborg, <u>Nucleonics</u>, <u>5</u>, No. 5, 16 (1949).

Table I

CARRYING OF TRACER BERKELIUM FROM SOLUTIONS OF VARIOUS OXIDIZING AND REDUCING STRENGTHS

Conditions for Oxidation	% Carried By Zirconium Phosphate*
3M HCl, reduced with Zn amalgam, 25°C.	5
3M HCl, saturated Br_2, 75°C., 15 min.	5
3M HCl, saturated Cl_2, 75°C., 15 min.	5
3M HNO_3, 75°C., 15 min.	5
3M HNO_3, 0.1M $NaBrO_3$, 0.2M H_3PO_4, 75°C., 5 min.	85
7M HNO_3, 0.1M $NaBrO_3$, 25°C., 15 min.	88
5M HNO_3, 0.1M $Na_2Cr_2O_7$, 75°C., 15 min., heated 15 min. at 75°C. after precipitation	89
0.015M Ce(IV), .015M Ce(III), 8M HNO_3, 75°C., 5 min.	56**
0.015M Ce(IV), 0.006M Ce(III), 8M HNO_3, 75°C., 5min.	69
0.015M Ce(IV), 8M HNO_3, 75°C., 5 min.	80

*Zirconium phosphate precipitations made under following conditions: 3M HNO_3 or 3M HCl, ~0.5M H_3PO_4, 0.2 mg/ml Zr(IV), solution heated a few minutes to allow complete precipitation.

**Cerium(IV) iodate used as carrier here and following experiments.

It is, of course, difficult to determine a thermodynamic "standard" oxidation potential from tracer experiments. Moreover, the activity coefficients of the aqueous actinide ions are not known. However, with the benefit of the wide experience extant for tracer experiments with the actinide elements, together with the fact that their formal oxidation potentials are known through experiments with macroscopic quantities, it is known that estimates of the formal potentials, based on tracer experiments of this sort, may be reasonably reliable. It can be seen from Table I that, in 8M nitric acid the oxidation potential corresponding to the Bk(III) ⟶ Bk(IV) change is very nearly the same as that for the corresponding change in cerium. It seems likely that berkelium is subject to the same type of complex ion formation as cerium and hence, like cerium, its oxidation potential must always be regarded with this in mind. The data, therefore, indicate a formal oxidation potential of ca. -1.6 volts for the Bk(III) ⟶ Bk(IV) couple.

It is a pleasure to acknowledge the advice and help in some of the experiments of B. B. Cunningham, Kenneth Street, Jr., and A. Ghiorso. This work was performed under the auspices of the U. S. Atomic Energy Commission.