either sodium chloride or sodium acetate. Empirical equations representing the data are developed.

As a rough approximation the partial molal volume of acetic acid in a solution containing electrolyte is the same as in an aqueous solution of the same total molality. This approximation does not hold in solutions of sodium chloride with molalities greater than 0.4.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF COLUMBIA UNIVERSITY]

Long Life Zirconium from Uranium 235 Fission

BY A. V. GROSSE[1] AND E. T. BOOTH

In our first paper on radioactive zirconium and columbium from uranium fission[1a] we described, outside of the 17.0-hour zirconium, also a long life zirconium, with a period of more than twenty days. In the following few months additional evidence was obtained, but publication was postponed due to other urgent atomic energy investigations. In the intervening years this fission product was investigated as part of the Plutonium Project,[2] but no details have appeared as yet. In 1940 Hahn and Strassmann[3] claimed to have discovered a 26-day zirconium. This they cancelled, however, in a short note in 1943[4] and simultaneously announced the long life zirconium to be described below. In the recently published Nuclear Physics Tables[5] the properties of our isotope have been inadvertently mixed with those of Hahn and Strassmann's 26-day zirconium. It thus seems worthwhile to publish our original findings.

Our zirconium proved to have a half-period of sixty-six days; this was followed for nearly three hundred days. As mentioned previously, it emitted electrons of about 0.25 MEV. energy. Chemical evidence proved unambiguously that the carrier of β-activity was the element zirconium. It produced a long life columbium isotope with very soft radiation, whose period was not determined.

Experimental Part

A typical experiment was carried out as follows: A 100-cc. solution of 70 g. of uranyl nitrate was bombarded by slow neutrons from the Columbia cyclotron on and off for a number of days. This was diluted to 1000 cc. of a 25% hydrochloric acid solution (by adding 588 cc. of 36% hydrochloric acid). Ten cc. of zirconium oxychloride solution, containing 135 mg. of zirconium dioxide, was added as carrier, together with various solutions containing a few milligrams each of stable isotopes to act as carriers for the radioactive fission products (*i. e.*, Rb, Cs, Sr, Ba, Y, La, Mo, Sb, Te, Ce, Cb, Br and I). On addition of 10-fold molar excess of phosphoric acid a fine, nicely settling precipitate of *zirconium phosphate* (ZrP_2O_7) was obtained, containing some insoluble columbic acid ($HCbO_3$).

This precipitate was washed with 25% hydrochloric acid and then purified twice from possible *natural* radioactive contaminations by addition of a few milligrams of Th, Bi, Pb, La + Ba and Fe as carriers. The radio-pure zirconium phosphate, still containing the added columbic acid and some iron oxide, was converted to zirconium dioxide by melting with a 10-fold quantity of sodium potassium carbonate in a platinum–gold dish; 143 mg. of zirconium dioxide and a trace of ferric oxide were obtained. These were further purified and fractionated as shown in Fig. 1; 19.0 mg. was painted on an aluminum disc (Al, 45) and measured. The rest was converted into acid soluble zirconium hydroxide (by sodium bisulfate melt and ammonia precipitation) and fractionally crystallized as $ZrOCl_2 \cdot 8H_2O$ from concentrated hydrochloric acid. The head or purest fraction of oxychloride was converted to oxide (56.5 mg. of snow white zirconium dioxide) and all of it painted on Al 47. Intermediate fractions were discarded. The residual zirconium was precipitated from the mother liquor, after diluting with hydrochloric acid, as a pure zirconium phosphate; all of it, equivalent to 16.7 mg. of zirconium dioxide, was painted on Al 48. The columbium was precipitated, from the sodium potassium carbonate-melt solution, with dilute acid; 51 mg. of columbium pentoxide, containing small amounts of zirconium dioxide, was obtained and painted on Al 46 for measurement.[5a] The scheme of the chemical separation is illustrated in Fig. 1. All measurements were made using an F. P. 54 amplifier and through 1 or 5 mil Al foil. The results of our measurements through 1 mil aluminum are plotted in Fig. 2. We see that all three zirconium preparations decay with the same period, namely, sixty-six days.

The specific activity *per 1.0 mg. of zirconium dioxide* of all three preparations, after correcting to *zero time*, was as follows:

Al 45, initial material $= 4.9 \times 10^{-3}$ div./sec.
Al 47, head fraction $= 4.9 \times 10^{-3}$ div./sec.
Al 48, tail end $= 5.2 \times 10^{-3}$ div./sec.

Thus, they are, within experimental error, identical. Zirconium is the only element, except ekatantalum (no. 91) and hafnium, which is precipitated from concentrated hydrochloric acid by phosphoric acid. Ekatantalum can be carefully separated from zirconium by the procedure we originally used to separate protactinium[6] and as was also subsequently demonstrated by the separation of ekatantalum[233] from thorium + n products.[7] Hafnium is only separated slowly from zirconium by tedious fractionation.[8] Thus the constancy of the specific activity, together with the other chemical evidence, is strong proof

(1) Present address: Houdry Process Corp., Marcus Hook, Pa.

(1a) A. V. Grosse and E. T. Booth, *Phys. Rev.*, **57**, 664–665 (1940).

(2) "Nuclei Formed in Fission," issued by the Plutonium Project, THIS JOURNAL, **68**, 2411–2442 (1946).

(3) O. Hahn and F. Strassmann, *Naturwissenschaften*, **28**, 548 (1940).

(4) O. Hahn and F. Strassmann, *ibid.*, **31**, 499–501 (1943).

(5) J. Mattauch, "Nuclear Physics Tables," Interscience Publishers, Inc., New York City, N. Y., 1946, p. 140.

(5a) Data on this columbium isotope will be published later. Hahn and Strassmann[4] give it a half life of fifty-five days.

(6) A. V. Grosse, *Ber.*, **61**, 233 (1928).

(7) A. V. Grosse, E. T. Booth and J. R. Dunning, *Phys. Rev.*, **59**, 322–323 (1941).

(8) G. v. Hevesy, "Recherches sur les propriétés du hafnium," Kopenhagen, 1925, p. 105.

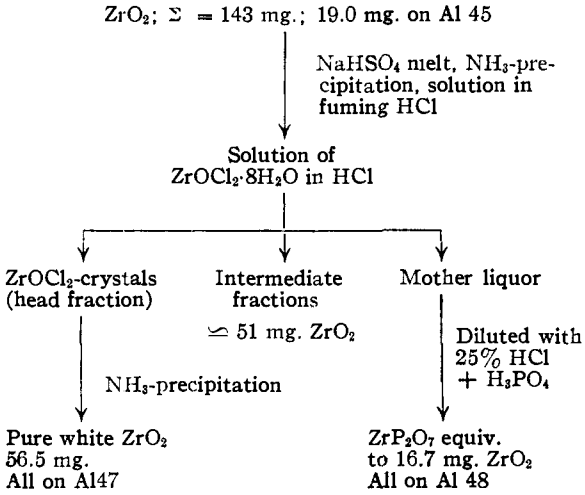


Fig. 1.—Purification and Fractionation of ZrO_2.

that the sixty-six-day activity is due to zirconium; hafnium is excluded both because of its high atomic mass and the relatively high intensity of our activity.

A blank run was made on the uranium solution we used in order to exclude any contamination from various possible cyclotron sources and targets; any possible contamination of the zirconium preparation was found to be below 1% of our activity.

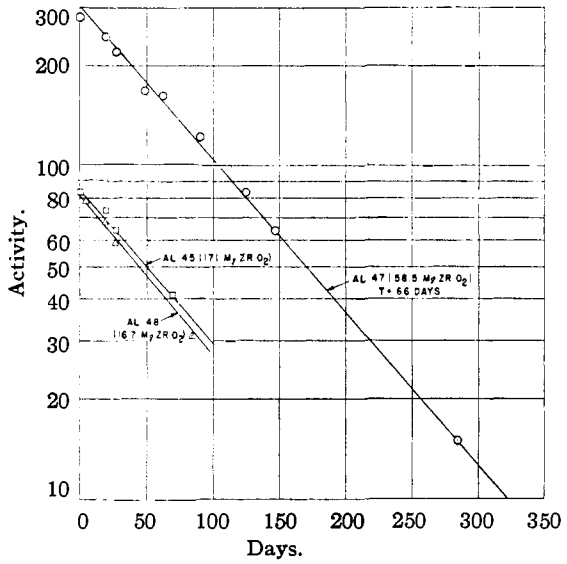
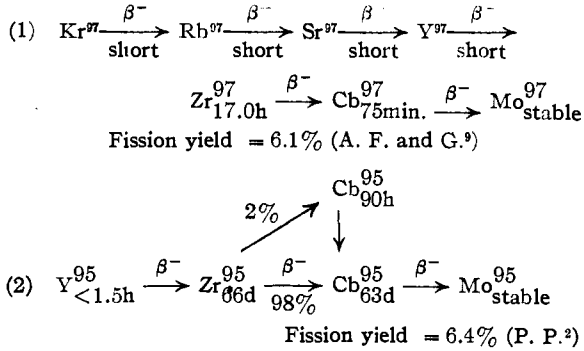


Fig. 2.—Zirconium of sixty-six days half period.

Discussion

Thus the existence of two zirconium isotopes of 17.0 hours and 66 days half-time seems assured. The fission yield of the first isotope was found to equal 6.1% in a joint investigation with H. Anderson and E. Fermi.[9]

Subsequently, these two isotopes have been confirmed by workers on the Plutonium Project.[2] Furthermore, their mass numbers have been established and the fission series determined as follows[10]:



Both in G. Seaborg's 1940 report[11] and the Nuclear Physics Tables[5] of 1946, the mass assignments are erroneous, namely, 95 for 17.0 hr. Zr and 75 min. Cb and 93 for the 66 day zirconium.

Hahn and Strassmann have withdrawn their claims[1] to a twenty-six day zirconium[4]; as we suspected earlier, it was very likely due to a contamination of their very weak preparation with UX.

Other radioactive zirconium isotopes from uranium fission are to be expected, since the 93 mass series ending in the stable Cb^{93} and the 97, 98 and 100 series, ending in the corresponding stable molybdenum isotopes, *should pass through* such radioactive bodies. Furthermore, all series from masses 90 to 100 should have high fission yield from 5.0% to a maximum of about 6.4% since they all lie on the light group *hump* of the fission curve.

However, no reliable information is available on such isotopes. The Plutonium Project (p. 2421) lists a Zr^{93} with a half time of 2.5 minutes as questionable and is left out of the otherwise well-known mass 93 series. It will be the object of future research to find these isotopes.

This work was carried out from February to August, 1940, in the Department of Physics of Columbia University. Pressure of National Defense Work prevented earlier publication.

Acknowledgments.—We wish to acknowledge the continued interest of Dean G. Pegram and Dr. John Dunning in this investigation.

Summary

A long life zirconium of 66-day half period is described as a product of uranium 235 fission.

Other zirconium isotopes from U-fission are critically reviewed.

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(9) H. Anderson, E. Fermi and A. V. Grosse, *Phys. Rev.*, **59**, 52–56 (1941).

(10) See ref. 2, p. 2439.

(11) G. Seaborg, *Chem. Rev.*, **27**, 239 (1940).