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Chemistry-Transuranic Elements

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HIGH ENERGY PROTON SPALLATION - FISSION OF URANIUM

R. L. Folger, P. C. Stevenson, and G. T. Seaborg

May 28, 1951

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Carbide and Carbon Chemicals Company (K-25 Plant)	15 - 16
Carbide and Carbon Chemicals Company (Y-12 Area)	17
Chicago Patent Group	18
duPont Company	19 - 23
General Electric Company, Richland	24 - 27
Hanford Operations Office	28
Idaho Operations Office	29 - 30
Iowa State College	31
Kellex Corporation	32
Knolls Atomic Power Laboratory	33 - 36
Los Alamos	37 - 39
Mound Laboratory	40 - 42
Naval Research Laboratory	43
New York Operations Office	44 - 45
North American Aviation, Inc.	46
Oak Ridge National Laboratory (X-10)	47 - 52
Patent Branch, Washington	53
Savannah River Operations Office	54
UCLA Medical Research Laboratory (Warren)	55
U. S. Naval Radiological Defense Laboratory	56
University of California Radiation Laboratory	57 - 60
University of Rochester	61 - 62
Wright-Patterson Air Force Base	63 - 64
Technical Information Service, Oak Ridge	65 - 79

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HIGH ENERGY PROTON SPALLATION - FISSION OF URANIUM

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May 28, 1951

ABSTRACT

The fission and spallation reactions caused in uranium by bombardment with high energy protons (340 to 350 Mev) were investigated. The reaction products were separated from the target by chemical processes and identified by their radioactive properties. The relative yields of the observed fission products were measured, and the results plotted as a function of mass number. Several of the spallation products were identified and their yields estimated.

An attempt was made to determine the most probable atomic number for a nuclide of given mass formed directly from fission. Studies were made of the relative yields along several isobaric chains as a function of atomic number. From these data predictions of the mass and charge of the fissioning nucleus are made.

Using the reaction $\text{Al}^{27}(\text{p}, 3\text{pn})\text{Na}^{24}$ of known cross section to monitor the bombarding beam, the formation cross sections for several fission product nuclides were measured. Values for these reference nuclides were used to transform the relative yields into formation cross sections. Integration over the range of mass numbers of the area under the curve of formation cross section as a function of mass number led to a value for the total fission cross section for uranium bombarded with high energy protons, assuming predominantly binary fission.

*Now at E. I. du Pont de Nemours and Co., Oak Ridge, Tennessee.

HIGH ENERGY PROTON SPALLATION - FISSION OF URANIUM

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I. INTRODUCTION

A. Summary of Previous Data on High Energy Fission

In recent years there has been considerable interest in the mechanism of fission induced by high energy particles (greater than a few Mev) as compared to that induced by low initial excitation. The greatest amount of work has been done with the target elements bismuth,¹ thorium,^{2,3} and uranium.^{3,4} High energy fission of other heavy elements from $Z = 73$ to $Z = 82$ has been observed.⁵ Batzel and Seaborg⁶ have announced the high energy fission of a number of medium weight elements.

The yield distribution of fission products has been studied by chemical separation techniques followed by identification of the nuclides through radioactivity measurements, and also by measurement of the kinetic energies of the fission fragments. The predominant characteristics of high energy fission which appear from these studies are:

- (1) A single peak is found in the yield versus mass distribution curve, indicating symmetric fission.
- (2) Evaporation of nucleons is evidenced by the mass number of the yield peak being less than one-half the mass of the target nucleus.
- (3) The kinetic energies of the fission fragments seem to be practically independent of the initial target nucleus excitation.

Predominantly symmetric fission has been reported by Goeckermann and Perlman¹ (bismuth with 190 Mev deuterons), O'Connor and Seaborg⁴

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(uranium with 380 Mev helium ions), and Jungerman and Wright³ (uranium with 90 Mev neutrons).^{*} At intermediate energies, the contribution of asymmetric fission is shown by the appearance of two peaks with a shallow dip between them. This effect has been observed by Newton² (thorium plus 38 Mev helium ions), and Jungerman and Wright³ (uranium plus 45 Mev neutrons).^{*}

In the high energy deuteron fission of bismuth, Goeckermann and Perlman¹ observed symmetric binary fission in which the mass of the nuclei having the peak yield was less than one-half the mass of the target nucleus. The mass difference indicated the evaporation of 10 to 12 nucleons. The relative yields of the fission product isobars seemed to indicate that the most probable primary products were those having the same charge to mass ratio as the fissioning nucleus. Yamaguchi,⁷ in a theoretical treatment of nuclear evaporation, has shown that for bismuth bombarded with 200 Mev deuterons, the half-width for neutron emission is greater than the half-width for fission until 10 to 11 neutrons have been emitted. In the case of uranium bombarded with 380 Mev helium ions,⁴ the peak mass was not well enough defined to demonstrate nuclear evaporation although the curve showed a strong possibility that such particle evaporation had occurred.

Measurements of fission fragment kinetic energies have been made by Jungerman and Wright,³ using ionization chamber techniques, and indirectly by Douthett,⁸ measuring the ranges of the fragments in aluminum. In bombarding uranium with 45 and with 90 Mev neutrons, Jungermann³ observed

^{*} Represents ionization chamber measurement of fragment kinetic energies.

the mean kinetic energies to be 79^{+} and 80 ± 2 Mev, respectively. Within the limits of experimental error, the ranges of fission fragments obtained by radiochemical separation from absorber foils were respectively the same for slow neutron fission^{9,10} of U^{235} , and the fission of natural uranium with 18 Mev deuterons.⁸ In the case of uranium plus 335 Mev protons,⁸ there is a systematic lowering of the observed fission fragment energies by about 6 to 8 Mev compared to slow neutron fission. Two explanations have been advanced for this lowering of observed kinetic energy.⁸ If evaporation of nucleons takes place to a significant extent, the mass of the fragment complementary to the observed fission fragment will be less than that of the comparable fragment in the case of slow neutron fission. The proportionately lighter fragment will carry off a relatively greater amount of the available energy, leaving less for the observed fragment. Another explanation is that evaporation of some charged particles leaves less coulombic potential, hence less total available kinetic energy.

These results suggest that the actual fissioning nucleus in each case is in a relatively unexcited state and that the high initial excitation energy is not transmitted as increased kinetic energy of the fragments.

B. Statement of the Problem

The purpose of this research was to investigate the fission and spallation reactions caused in uranium by bombardment with high energy protons (340 to 350 Mev). The reaction products were separated from the target by chemical processes and identified by their radioactive properties. Measurement was made of the relative yields of the observed fission products and the results plotted as a function of mass number (Figure 1).

An attempt was made to determine the primary products (those formed directly from fission with highest probability for a given mass) for various mass numbers. An estimate of the location of primary products with respect to the stable nuclides may be made by observing the variation of independent yield (formed directly in fission rather than by growth from a radioactive "parent") with mass for a given element in the region of interest. A more accurate determination of primary products may be made by determining the independent yields of isobaric nuclides as a function of atomic number.

In contrast to the case of bismuth¹ the fission instability of the heavy elements in the region of uranium is such that fission is energetically possible at low excitation energies without the necessity of the previous evaporation of large numbers of neutrons to give a more favorable Z^2/A parameter. However, at the high excitations obtainable with 340 Mev protons, it is possible for many nucleons to be evaporated prior to fission.¹ It was of interest therefore to determine the most probable fissioning nucleus under these conditions. From the work of O'Connor and Seaborg,⁴ the yield versus mass curve might be expected to show a distinct symmetry about a single peak. This would suggest that symmetric binary fission is the most probable mode of fission. When the most probable fission is symmetric, the mass of the peak of the yield versus mass curve should be one-half the mass of the fissioning nucleus. When the Z/A ratio is constant as in the case of bismuth fission,¹ a homogeneous fluid model of the fissioning nucleus may be chosen. The ratio Z/A of the primary fission products may then be used to determine the atomic number of the fissioning nucleus.

The excited nuclei formed in the target by the bombarding beam do not necessarily undergo fission. In some cases the evaporation of nucleons may proceed to give spallation products which do not fission. An attempt was

made to identify several spallation products and make a rough estimate of their yields in an effort to determine what fraction of the total reactions proceeded by this path.

The cross section for the reaction $\text{Al}^{27}(\text{p}, 3\text{pn})\text{Na}^{24}$ with 340 to 350 Mev protons was measured by comparing it to the cross section for the reaction $\text{C}^{12}(\text{p}, \text{pn})\text{C}^{11}$ which has been measured by Aamodt, Peterson, and Phillips.¹¹ By monitoring the bombarding beam with aluminum foils it becomes possible to measure the formation cross sections for several reference mass nuclides. Using these values, the yield versus mass curve could be transformed into a "formation cross section versus mass" curve. Integration under this curve makes possible the determination of the fission cross section for uranium with 340 Mev protons, assuming predominantly binary fission.

II. FISSION PRODUCT YIELDS

A. General Considerations

The quantity $IN\sigma$ (where N represents the number of atoms exposed to a bombarding beam of intensity I), hereinafter referred to as the independent rate of formation, R , (independent of the duration of the bombardment) is proportional to the cross section for formation of the radioactive species under consideration. Most of the earlier determinations in this work were made relative to the independent rate of formation of Ba^{140} and its precursors since no absolute formation cross sections had been measured at that time. The initial yield results are therefore expressed relative to the independent rate of formation of Ba^{140} and its precursors, defined as 1.00. The "relative yield" is defined to be the ratio of the cross section of formation of the nuclide in question to the cross section of formation for Ba^{140} and its precursors.

Chemical Techniques.-- The final sample for measuring the disintegration activity of a radioactive nuclide does not in general consist of 100 percent of the amount of this species produced in the bombardment (allowing for decay). To correct for the amount of active species lost during the chemical separation procedure, it is customary to mix with the active species a known amount (usually 1 to 10 mg) of the inactive element, the carrier, whose isotopes are being considered. When due precautions have been taken to ensure equilibrium exchange, the percent recovery of the active species is assumed to be identical with the percent recovery of the carrier material.

In designing a chemical separation procedure it is necessary to consider the estimated radioactive yield of the desired nuclide in relation to the estimated yields of the most likely contaminants.

Detecting Instruments.-- Alpha emitting samples were measured either in a proportional counter or in an ionization chamber apparatus. Alpha energies were determined by means of an alpha pulse analyzer.¹²

Samples emitting beta and gamma radiation were counted by means of end-window Geiger-Müller tubes. When this work was begun, the tubes available were of the argon-alcohol type. For the more recent work, end-window tubes filled with a mixture of argon and chlorine (Amperex, Type 100-C) were used. These tubes show greater stability of counting characteristics than the argon-alcohol tubes, and are capable of measuring counting rates a factor of ten higher than the argon-alcohol tubes could measure.

A crude magnetic beta ray spectrometer of low resolving power was used to differentiate between positive and negative electrons, and to

measure maximum beta energies in some cases.

Backscattering.-- Correction factors for the scattering of beta particles into the counter from the backing material on which the sample is mounted have been empirically determined by several workers.¹³⁻¹⁵ The amount of backscattering depends primarily upon the thickness and atomic number of the backing material. The scattering is relatively insensitive to beta energy in the range 0.6 to 3 Mev.^{14,15} In most of our work, the sample considered and the Ba¹⁴⁰ monitor were mounted on similar backings so that for relative yields the backscattering correction cancelled out.

Self-Scattering and Self-Absorption Corrections.-- Since the radioactive samples in many cases were of finite mass, it was necessary to determine the loss of gain of apparent activity in passing through the mass of the sample. There is a loss of apparent activity due to absorption in the material of the sample. Scattering of beta particles and electrons by the material of the sample causes an apparent increase in the activity. Some preliminary experiments were performed to determine empirically the combined self-absorption and self-scattering corrections.^{16,17} The absorbing power of sample material for particles changes only slowly with the atomic number, but the scattering power increases markedly. In some cases the scattering effects were so great that a net increase in apparent counting rate was obtained even for several milligrams per square centimeter of sample thickness.

Air Window Absorption.-- The loss of activity by absorption in the air between the sample and the counter window, and in the window itself was determined by straight line extrapolation of aluminum and/or

beryllium absorption curves whose initial portions were carefully measured using thin absorbers.

Counting Efficiencies.-- In determining yields of various nuclides it was necessary to make some assumptions regarding relative counting efficiencies. For beta particles and electrons a counting efficiency of 100 percent was assumed with the argon-alcohol filled tubes. The calculated counting efficiencies used for electromagnetic radiation, based on absorption in the gas of the counter tube, were 0.5 percent for energies from 20 kev to 0.5 Mev, and 1 percent per Mev thereafter for argon-alcohol filled tubes.¹⁸ The ratio of the over-all efficiency of the argon-chlorine (Amperex) tubes to the argon-alcohol tubes for the same geometry was determined to be 45 percent by counting a number of samples having beta and electromagnetic radiations of various energies.¹⁹

Effective Geometry.-- The effective geometry is related to the solid angle subtended by the sensitive volume of the counter tube at various distances from the sample. The sample holders used in the Geiger counting had five positions varying from 0.3 to 6.7 cm from the tube window. An attempt was made to count the monitor sample in the same position as the sample of the nuclide whose relative yield was being determined. Where such an arrangement was not practical initially, due to too great a difference in the counting rates of the samples, the "geometry" ratio would be determined empirically when the counting rates were more nearly equal. This ratio was not a true geometric ratio because of increased air absorption at greater distances from the counter window. For cases in which the absorption characteristics of a particular beta spectrum were rather well known so that air absorption

corrections could be applied, measurements of the true geometric ratios between various positions were made.

B. Observed Fission Product Nuclides

The chemical procedures used to isolate the various elements are discussed in Appendix I.

Sodium.-- From a uranium target prepared with extreme care to eliminate any light element surface contamination, the isolated sodium fraction showed a beta activity of 15 hour half-life in amount larger than could be accounted for by impurities in the uranium. The decay was followed for four half-lives without observing any deviation due to radioactive impurities. Aluminum absorption measurements of the beta radiation showed the 1.4 Mev beta energy of Na^{24} . *

Manganese.-- In the manganese fraction separated after an eight hour bombardment of a uranium target, a 5.8 day activity was observed. The absorption characteristics and half-life corresponded to those observed for Mn^{52} formed by spallation of iron with 340 Mev protons.²⁰ The amount of Mn^{52} produced could be accounted for by the known amounts of iron and nickel impurities in the uranium target.

Iron.-- The iron decay measurements showed two major components. One was the expected 46 day Fe^{59} . The shorter component, having a half-life of about 8.4 hours, seems to be a new activity. Decay measured through 222 mg/cm² of aluminum (to block the particulate radiation of Fe^{59}) showed the 8.4 hour activity. No growth was observed (limit detectable, 20 minutes). This new activity is probably due to Fe^{60} .

Aluminum absorption measurements of the 46 day activity showed the soft beta radiation of Fe^{59} . Aluminum absorption measurements on the

*Unless otherwise indicated, values of the half-life and beta energy for the various nuclides were obtained from either the "Table of Isotopes"²¹ or the "Chart of the Nuclides."²²

8.4 hour activity showed a beta particle of about 1.5 Mev energy. The sample was measured on a crude magnetic beta ray spectrometer. The 8.4 hour activity showed negative beta radiation. No positrons were observed.

Cobalt.-- Decay measurements of the cobalt fraction showed a component of 1.7 hours, presumably due to Co^{61} . Aluminum absorption measurements of the 1.7 hour activity showed a beta energy of about 1.3 Mev.

Nickel.-- The decay of nickel showed components of 2.6 hours and 56 hours, presumably Ni^{65} and Ni^{66} , respectively. Aluminum absorption measurements of the 56 hour Ni^{66} showed the 2.9 Mev beta particle of 4.3 minute Cu^{66} in equilibrium.

Copper.-- Three isotopes of copper were identified. The 3.4 hour Cu^{61} was observed by following the decay of its positrons on a crude beta ray spectrometer. The 12.9 hour Cu^{64} was also seen in this manner as well as by resolution of the decay curve obtained with a conventional Geiger counter. Sixty hour Cu^{67} was clearly seen in the beta decay curve.

Fermi-Kurie plots of the crude beta spectrometer positron data showed the 1.2 Mev β^+ of Cu^{61} and the 0.66 β^+ of Cu^{64} . Aluminum absorption measurements, taken after the 12.9 hour activity had decayed out, showed the 0.6 Mev β^- of Cu^{67} .

Zinc.-- Observation of the decay of the zinc samples showed a half-life of 49 hours. A growth corresponding to a daughter half-life of 14 hours was observed, indicating the presence of 49 hour Zn^{72} with 14 hour Ga^{72} daughter.

Arsenic.-- Decay of the arsenic samples observed through 350 mg/cm² of aluminum (to block the particulate radiation of As^{77}) showed an

activity of 26.8 hours half-life. Decay without absorber showed the 40 hour activity of As^{77} .

Selenium.-- The predominant activity in the selenium samples was the 59 minute Se^{81m} with the 17 minute Se^{81} in equilibrium. It was possible to detect the 25 minute Se^{83} both by resolution of the decay curve and by observing the 2.4 hour Br^{83} daughter in the decay measurements. Twenty-four hours after bombardment, the decay curve showed essentially no activity other than the 2.4 hour Br^{83} .

Aluminum absorption measurements on the 59 minute activity showed the 1.5 Mev beta particle of Se^{81} .

Bromine.-- The bromine decay curves showed mainly 2.4 hour and 35 hour components when measured without absorber. Decay measured through 490 mg/cm^2 of aluminum showed components of 4.4 hour and of 34 minute half-life after subtraction of a 35 hour component due to the penetrating radiation of Br^{82} . Decay measured through 750 mg/cm^2 of aluminum showed a component of 34 minute half-life and a residium of 4.4 hour and 35 hour activities. The relative counting efficiency of the 4.4 hour activity was considerably reduced by the increased absorber. Aluminum absorption measurements of the 2.4 hour activity showed a 1 Mev beta particle.

From the evidence we conclude that Br^{80m} , Br^{82} , Br^{83} , and Br^{84} are formed as fission products with Br^{83} being produced in highest yield.

Rubidium.-- The rubidium sample showed an activity of 19.5 day half-life, presumably Rb^{86} . The sample was not isolated soon enough to detect any of the shorter lived rubidium isotopes. Aluminum absorption measurements on the rubidium activity showed a 1.8 Mev beta particle.

Strontium.-- From decay measurements a 9.7 hour strontium activity was observed. A 60 day yttrium activity was chemically separated from the strontium sample, indicating the presence of Sr^{91} . Another strontium sample, from which yttrium had been removed a week after bombardment of the target, showed an activity of 54 day half-life. This was thought to be Sr^{89} .

Aluminum absorption measurements on the 54 day activity showed the characteristic 1.5 Mev beta particle of Sr^{89} . The background due to electromagnetic radiation was negligible.

Zirconium.-- The zirconium decay showed a 17 hour activity which grew a 69 minute daughter, presumably due to Zr^{97} and Nb^{97} . After decay of the Zr^{97} , a decay line of predominantly 65 day half-life (Zr^{95}) was seen.

Niobium.-- Four major species were identified in the niobium decay: 68 minute Nb^{97} ; an activity of approximately 23 hours, probably Nb^{96} ; 90 hour Nb^{95m} obtained by analytical treatment of the counting data; and 37 day Nb^{95} .

Molybdenum.-- The only activity observed in the molybdenum fraction was the 67 hour Mo^{99} .

Ruthenium.-- Decay measurement showed a 4.4 hour activity and longer components. After allowing one year for intermediate activities to die out, decay for a period of one year showed a one year activity. When the activity due to this component was subtracted from the earlier data, an activity of approximately 43 day half-life was observed. Subtraction of this in turn showed a 37 hour activity, indicating the presence of 4.4 hour Ru^{105} decaying to 37 hour Rh^{105} . The 43 day activity

was presumed to be Ru^{103} .

Aluminum absorption measurements on the one year activity showed the characteristic hard beta particles of the Rh^{106} daughter in equilibrium with 1.0 year Ru^{106} .

Palladium.-- Two palladium activities were observed directly, 21 hour Pd^{112} and 14 hour Pd^{109} . The formation of 26 minute Pd^{111} was demonstrated by the separation of 7.5 day Ag^{111} from a portion of the target immediately after bombardment and from a second portion after an interval of three to four hours. The specific activity of Ag^{111} was significantly higher in the second portion than in the first, indicating its formation by the decay of Pd^{111} .

Decay was measured without absorber, through 80 mg/cm^2 of aluminum (to block the beta particles of Pd^{112}), and through 490 mg/cm^2 of aluminum (blocking the beta particles of Pd^{112} and Pd^{109} , but allowing the radiation of 3.2 hour Ag^{112} in equilibrium with Pd^{112} to be counted). Growth of the 3.2 hour Ag^{112} was observed.

Silver.-- Decay through 1380 mg/cm^2 aluminum (to block all particulate radiation from silver isotopes except that of Ag^{112}) showed the 3.2 hour Ag^{112} . Decay without absorber on a sample separated very soon after bombardment (to minimize growth of 3.2 hour Ag^{112} from 21 hour Pd^{112}) emphasized the 5.3 hour Ag^{113} . The 7.5 day Ag^{111} was clearly seen, and shown to be formed (see above) as a primary fission product, its independent yield being 18-20 percent of the total observed β^- chain. Decay followed over a period of ten months showed an activity of 250-270 days, presumably Ag^{110} .

The formation of 20 minute Ag^{115} was shown by separating 53 hour Cd^{115} from a portion of the target immediately after bombardment and from a second portion after an interval of about four hours. The specific activity of Cd^{115} separated from the second portion was significantly higher than that from the first portion, indicating its formation by decay of Ag^{115} .

A sample of silver was initially separated from cadmium, then allowed to decay. Cadmium separated from this sample after four hours showed a 53 hour half-life with no indication of a 43 day component. This indicates that Ag^{115} decays predominantly to the Cd^{115} ground state rather than to $\text{Cd}^{115\text{m}}$.

Aluminum absorption measurements on the 3.2 hour activity showed the characteristic 3.6 Mev beta particle of Ag^{112} . Measurements on the 7.5 day activity showed the 1 Mev beta energy of Ag^{111} . The background due to electromagnetic radiation was less than 0.05 percent of the initial activity. Correcting for the difference in counting efficiencies, this means that any 8.6 day Ag^{106} must be present in an amount less than 5 percent of that of Ag^{111} .

Cadmium.-- Decay through 946 mg/cm^2 of beryllium (to block all particles of energy less than 1.9 Mev) showed evidence of the 49 minute $\text{Cd}^{111\text{m}}$ and indicated the possible presence of 6.7 hour Cd^{107} . Decay of the beta radiation showed 2.8 hour Cd^{117} , 53 hour Cd^{115} , and 43 day $\text{Cd}^{115\text{m}}$. There was a very long lived component which suggested the presence of 470 day Cd^{109} . Aluminum absorption measurements showed the 1.1 Mev beta particle of the 53 hour Cd^{115} .

Tin.-- Decay measurements showed components of about 27 hour and of 9.5 day half-life and a longer component, presumably of 130 day half-life. These seem to be Sn^{121} , Sn^{125} , and Sn^{123} , respectively. The other isomer of each mass number was not observed.

Tellurium.-- Of the many components in the tellurium decay curve, it was possible to resolve out only the 30 hour Te^{131m} and its 8 day I^{131} granddaughter.

Cesium.-- The predominant activity in the cesium fraction was the 13 day Cs^{136} . Aluminum absorption measurements of this activity showed the characteristic 0.3 Mev beta energy of Cs^{136} . Comparison of the activity observed through aluminum absorbers and through beryllium absorbers indicated soft electromagnetic radiation (of the order of K x-rays in this region) present to the extent of about 15 percent of the particulate radiation. This indicates relatively good yields of neutron deficient cesium isotopes decaying by orbital electron capture.

Barium.-- Most of the bombardments were interrelated by measuring the amount of 12.8 day Ba^{140} produced, and using this as an internal monitor. In most cases the barium was not separated from radium. In these cases, the sample was counted through enough aluminum absorber to prevent any alpha particles emitted by radium or its daughters from reaching the counter tube. In addition to observing its half-life, Ba^{140} was identified by observing the growth of its 40 hour La^{140} daughter.

A sample of the radioactive barium was analyzed in the mass spectrograph.* The emulsion side of the collector plate was placed against the emulsion of a second plate and the radioactive species allowed to decay.

*Mass spectrographic analysis by F. L. Reynolds of this laboratory.

for a period of about two weeks. Lines on the second or "transfer" plate indicated radioactive barium isotopes of masses 131, 133, 135, and 140 in comparable yields. An approximately 10 day activity was observed in a cesium sample separated from a purified barium sample some time after bombardment.

Although Ba^{131} has approximately the same half-life and may be present in yields of the same order of magnitude as Ba^{140} , the activity of $\text{Ba}^{131}\text{-Cs}^{131}$ detected by the Geiger tube is less than 1 percent of the corresponding activity of $\text{Ba}^{140}\text{-La}^{140}$ because of the large difference in counting efficiencies.

Components of 29 to 39 hours having soft particle radiation were observed in the decay curves. These probably represent a mixture of $\text{Ba}^{133\text{m}}$ and $\text{Ba}^{135\text{m}}$. An 85 minute component, presumably Ba^{139} , was also observed. In a sample of barium separated from radium on an ion-exchange column, the 85 minute, 29 to 39 hour, and 12.8 day components were observed. The positrons of 2 hour Ba^{129} were not observed on a crude beta ray spectrometer measurement of the column separated barium.

Lanthanum.-- Decay curves showed essentially a single component, the 40 hour La^{140} , over a period of 8-9 half-lives. Decay of the radiation which passed through 946 mg/cm² of beryllium (to block the particles and give other possible electromagnetic radiation a more favorable counting efficiency relative to La^{140}) gave a curve essentially parallel to the curve taken without absorber. Since the final separation of lanthanum was not accomplished until 56 hours after bombardment, the possibility of formation of nuclides of shorter half-life in comparable yield is not excluded.

Aluminum absorption curves of the 40 hour activity compared closely with absorption curves of the radiations from the 40 hour β^- daughter of Ba^{140} . From the absorption curves, the counting rate was corrected for air and window absorption, and for the contribution of the electromagnetic radiation. The disintegration rate was calculated from this corrected counting rate.

Calculations based on the relative yields of Ba^{140} , La^{140} , and Nd^{140} (explained in Section III) show that approximately 30 percent of the total mass number 140 yield is formed as La^{140} .

Cerium.-- Decay curves showed components of approximately 35 hours and approximately 30 days with a component of intermediate half-life. Analysis of the data indicated Ce^{143} with Pr^{143} daughter, and Ce^{141} . Decay over a period of about six months indicated the presence of 275 day Ce^{144} .

Comparison of the number of x-rays emitted by the long lived activity with the number from Ce^{144} tracer obtained from slow neutron fission of uranium indicated the presence of 140 day Ce^{139} in our sample. Aluminum absorption measurements on the long lived component showed two beta components which could be attributed to Ce^{144} and the 17 minute Pr^{144} in equilibrium.

Praseodymium.-- Observation of the decay through 406 mg/cm^2 of aluminum showed a 19 hour half-life. Observation of the decay without absorber showed two components, one of 13.5 day half-life, the second (by subtraction) of half-life 16 to 19 hours. Aluminum absorption measurements on the 19 hour activity showed hard beta radiation of 2.3 Mev energy and indicated a soft component of about 0.6 Mev energy in about

20 percent abundance. After decay of the 19 hour activity, aluminum absorption measurements of the 13.5 day activity showed a particle of 0.92 Mev maximum energy. On the basis of the decay and absorption measurements, it was concluded that Pr^{142} and Pr^{143} were both present in good yield.

Pr^{142} is a shielded nuclide; consequently, its independent yield was obtained directly. The independent yield of Pr^{143} was obtained by removal of the 33 hour Ce^{143} parent from the rare earth group within two hours after bombardment. From the yield curve (Figure 1) it is expected that the total yield of products of mass number 143 will be less than the total yield of products of mass number 142. Since in the case of these two isotopes the ratio of the yield of Pr^{143} to that of Pr^{142} was about 1.7, the Pr^{143} represents a greater fraction of the total mass number 143 yield than the Pr^{142} does of its total mass number yield. This indicates that whereas the most probable primary charge for a given mass is on the neutron excess side for isotopes of the lighter elements, the trend is for the most probable primary product to be much closer to stability for the higher mass chains.

Neodymium.-- Observation of the decay through 407 mg/cm² of beryllium (sufficient to block the beta particles of Nd^{147}) showed two components. After subtraction of the 11 day tail due to the gamma ray of Nd^{147} , a 3.3 day decay was found. This is due to the activity assigned to Nd^{140} by Wilkinson and Hicks.²³ Decay measurements without absorber showed the 11 day half-life of Nd^{147} for over three half-lives. Aluminum absorption curves showed the characteristic beta particle energy of Nd^{147} . Since less than 2 percent of the initial total activity could be attributed

to Nd^{140} , this activity did not interfere and was not characterized by absorption. Its counting efficiency was calculated from the data of Wilkinson and Hicks.²³

Calculations based on the relative yields of Ba^{140} , La^{140} , and Nd^{140} show that approximately 7.5 percent of the total mass 140 yield is formed as Nd^{140} .

Promethium.-- Decay was observed both without absorber and through 485 mg/cm² of aluminum (sufficient to block the beta particles of Pm^{149}). The decay without absorber showed components of approximately 13 hours, of 47 hours, and of about 43 days. Decay of the radiations transmitted through the absorber showed components of 47 hours (the gamma ray of Pm^{149}), 5.3 days, and 43 days. Of the activities, only the 47 hour Pm^{149} and the 5.3 day Pm^{148} have been assigned. A 12.5 hour promethium activity has previously been reported, but no mass assignment was given. The 43 day activity represents a previously unreported nuclide.

Absorption of the radiations of the 47 hour activity showed a single beta component of about 1.1 Mev energy. This is the reported maximum energy for the beta particles of Pm^{149} . After decay of the 47 hour and 5.3 day components, absorption measurements of the 43 day activity were made. Aluminum absorption showed two beta components of energies about 0.5 Mev and about 2.3 Mev. The hard component was present to only 5 to 10 percent abundance. The sample was also measured on a crude beta ray spectrometer which showed (from a Fermi-Kurie plot of the data) β^- components of 0.6 and 2.4 Mev. The electromagnetic background of the aluminum absorption curve was of the order of 3 percent. After blocking the particulate radiation with beryllium absorber, the electromagnetic

component was absorbed in copper. No K x-rays of neodymium (which have a half-thickness of 165 mg/cm² in copper) were observed. Absorption of the electromagnetic radiation in lead showed a half-thickness of 7.5 g/cm² which corresponds to a gamma ray of approximately 0.9 Mev energy.

The yield of the shielded Pm¹⁴⁸ is only about 1 percent of that for the Pm¹⁴⁹ which represents the total β^- chain for its mass. The yield of the 43 day promethium is about 10 percent of that for Pm¹⁴⁹. On the basis of yield and the fact that this activity was not reported formed in slow neutron fission or by Nd¹⁵⁰(n, γ) or (p,n) reaction, a tentative assignment of the 43 day activity to Pm¹⁴⁶ is made.

Samarium.-- The samarium decay showed components of about 10 hours and of 47 hours, the 47 hour component being quite prominent. After decay of this activity, a 15-16 day line was observed. Aluminum absorption measurements of the 47 hour activity indicated a beta particle of about 0.8 Mev energy. In the absorption measurements the 2.4 Mev β^- of Eu¹⁵⁶ was also observed.

The principal activities found in the samarium fraction were thus the 47 hour Sm¹⁵³ and the 10 hour Sm¹⁵⁶ with its 15.4 day Eu¹⁵⁶ daughter. The yield of Sm¹⁵⁶ relative to Sm¹⁵³ was only 27 percent. The yield of Sm¹⁵³ represents the entire β^- chain for mass 153 whereas Eu¹⁵⁶ is expected to be a large contributor to the mass 156 yield.

Europium.-- The principal europium activity seen was the 15.4 day Eu¹⁵⁶. Aluminum absorption showed the characteristic 2.4 Mev β^- of Eu¹⁵⁶.

Terbium.-- The terbium decay curve resolved roughly into two components, the longer of which had a half-life of 74 days. The shorter component was a mixture of activities with half-lives between 5 and 7 days

and a shorter one. Decay was observed without absorber and also through 183 mg/cm² of beryllium (sufficient to block the 0.5 Mev β^- particles of Tb¹⁶¹). After subtraction of the 74 day residuum, the decay through beryllium showed strong indication of a 5.1 day activity. The decay observed without absorber showed a mixed activity with a 6.8 day activity predominating after subtraction of the 74 day component. These observations indicate the formation of Tb¹⁶⁰ and Tb¹⁶¹, and the probable formation of Tb¹⁵³ and Tb¹⁵⁶.

In the terbium fractions separated 12 to 14 hours after bombardment, traces of alpha activity were observed. A sample submitted to Mr. J. O. Rasmussen for alpha pulse analysis showed alpha energy and decay corresponding to 4.5 hour Tb¹⁴⁹.

Dysprosium.— The chief component observed in the dysprosium decay was the 80 hour Dy¹⁶⁶. A long lived activity was also observed, but it was not possible to determine its half-life. Aluminum absorption measurements on the equilibrium mixture showed the 0.4 Mev beta particle of Dy¹⁶⁶ and the 1.9 Mev beta particle of the Ho¹⁶⁶ daughter.

Calculations based on the relative yields of Dy¹⁶⁶, Ho¹⁶⁶, and Yb¹⁶⁶ (see Section III) indicate that 2.54 percent of the total mass 166 yield is formed as Dy¹⁶⁶.

Holmium.— The major component observed in the holmium decay was the 27 hour Ho¹⁶⁶. The decay was followed through eight half-lives. The activity remaining as long lived component was less than 0.02 percent of the Ho¹⁶⁶ activity present at end of bombardment. Aluminum absorption measurements showed the approximately 1.9 Mev beta energy of Ho¹⁶⁶. The 7 day activity presently assigned to Ho¹⁶³ was not observed in our

holmium sample in a resolvable amount. This may indicate that the 7 day holmium is shielded, and hence should be assigned to Ho^{162} .

Calculations based on the relative yields of Dy^{166} , Ho^{166} , and Yb^{166} indicate that 4.7 percent of the total mass 166 yield is formed as Ho^{166} .

Erbium.-- The erbium sample first showed growth, which was identified as a holmium activity from the plot of the radioassay data (see Appendix I, Recovery and Chemical Yield of Rare Earths). The samples of column elutriant containing erbium carrier showed a growth of activity while those samples taken after elution of the erbium but before elution of the holmium carrier showed rapid decay. This indicated a new erbium activity decaying by orbital electron capture and/or positron emission to a short lived holmium activity. Decay was observed without absorber and also through 99.7 mg/cm² of beryllium (to block the beta particles of Er^{169}). Two new activities were observed in the decay of activity transmitted through absorber; one of about 17 hour half-life and the other of 65 hour half-life. The decay without absorber showed a mixture of these activities and a component of 9.4 day, the Er^{169} .

The growth observed corresponded to a 4.5 hour half-life for the daughter activity. The holmium activity²⁴ of this half-life is assigned to Ho^{161} . The new erbium activities are probably $\text{Er}^{160,161}$ and Er^{163} . The data are not sufficient to match the activities to definite mass numbers.

Thulium.-- Decay measurements without absorber showed an approximately 10 day activity prominently. Observation of the decay through approximately 40 mg/cm² of aluminum and through approximately 60 mg/cm² of beryllium emphasized an activity of two to three days half-life. These

absorbers blocked the conversion electrons of 9.6 day Tm^{167} . The 9.6 day activity was masked to such an extent by the absorbers that it was not resolvable graphically from the shorter activity. Since an activity on the neutron deficient side of stability in this region would be expected to have about the same counting efficiency as the 9.6 day Tm^{167} , it is felt that the two to three day activity represents a negative beta transition, possible Tm^{172} .

Ytterbium.-- The ytterbium decay curve showed components of 32 days and 62 hours. The sample showed growth corresponding to a 7.7 hour daughter activity. The samples of column elutriant containing ytterbium carrier showed this growth of activity while those samples taken after elution of the ytterbium but before elution of the main body of thulium showed a decay of about eight hours half-life. The new ytterbium activity is thus shown to decay to a thulium activity. From the observed growth and an estimate of the time of separation from thulium, the counting efficiency of the ytterbium parent was found to be small compared to the thulium daughter. On the basis of the assignment of the 7.7 hour thulium activity²⁵ to Tm^{166} , the new 62 hour ytterbium activity is assigned to Yb^{166} .

Aluminum absorption measurements on the 62 hour activity showed the presence of conversion electrons, a hard beta particle, and electromagnetic radiation background. The relative abundance of electrons and hard beta particles (2 Mev) compared favorably with those reported for the particles²⁵ from Tm^{166} . Beryllium and copper-beryllium absorption measurements of the 32 day activity showed electrons, x-rays, and gamma rays comparable to some of those reported for 32.5 day Yb^{169} . Ninety-nine

hour Yb^{175} was not detected either by decay or absorption measurements.

Isobaric chain yield calculations indicated that 13.5 percent of the total yield of mass 166 was formed as Yb^{166} . The most probable primary charge for the nuclide of this mass is $Z = 71$.

C. Tabulation of Observed Yields

The yields of selected fission products measured relative to the yield of Ba^{140} (and its precursors) are given in Table I below. By definition, the relative yield, Y_R , of Ba^{140} (including its precursors) is 1.00.

Formation cross sections were measured for a number of nuclides including their precursors (i.e., total β^- chains). By means of these, the relative yield values ($Y_R = 1.00$ corresponds to $\sigma = 23.5$ mb) given in Table I below were converted to formation cross section values. Integration of the yield versus mass curve (Figure 1) in terms of the formation cross sections indicates a total fission cross section of 2.0 barns for uranium with 340 to 350 Mev protons.

Table I
Relative Yield of Fission Products ($\text{Ba}^{140} = 1.00$)

Mass Number	Nuclide Measured	Class*	Y_R
24	Na ²⁴	2 ✓	0.0021
59	Fe ⁵⁹	2 ✓	0.0078
65	Ni ⁶⁵	2 ✓	0.024
66	Ni ⁶⁶	2 ✓	0.027
67	Cu ⁶⁷	2 ✓	0.091
72	Zn ⁷²	2 ✓	0.090
76	As ⁷⁶	1	0.0091
80	Br ^{80m}	1	0.015
81	Se ^{81m}	3	0.34
82	Br ⁸²	1	0.067
83	Se ⁸³	3	0.22
	Br ⁸³	3 } ✓	0.16
84	Br ⁸⁴	3	0.14
86	Rb ⁸⁶	1	0.59
89	Sr ⁸⁹	3	1.4
91	Sr ⁹¹	3	1.6
92	Sr ⁹²	3	1.7
103	Ru ¹⁰³	3	1.8
106	Ru ¹⁰⁶	3	2.2
109	Pd ¹⁰⁹	3	0.19
111	Pd ¹¹¹	3 } ✓	1.76
	Ag ¹¹¹	3 } ✓	0.44
112	Pd ¹¹²	3	0.22
115	Cd ¹¹⁵	3 } ✓	1.46
	Cd ^{115m}	3 } ✓	0.51
131	Te ^{131m}	3	0.25
136	Cs ¹³⁶	1	0.25
139	Ba ¹³⁹	3	1.8
140	Ba ¹⁴⁰	3	1.00
	La ¹⁴⁰	1 } ✓	0.48
	Nd ¹⁴⁰	3 } ✓	0.18
142	Pr ¹⁴²	1	0.33
143	Pr ¹⁴³	1	0.55
147	Nd ¹⁴⁷	3	1.4
153	Sm ¹⁵³	3	0.19
156	Sm ¹⁵⁶	3 } ✓	0.05
	Eu ¹⁵⁶	3 } ✓	0.12
166	Dy ¹⁶⁶	3 } ✓	0.0019
	Ho ¹⁶⁶	1 } ✓	0.0020
	Yb ¹⁶⁶	3 } ✓	0.030
193	Os ¹⁹³	3	0.00043
~198	Au ^{198,199}	3	0.00094
224	Ra ²²⁴	3	0.12
236	(p,3n) reaction**		0.51

*Class 1 Independent yield or shielded nuclide
 Class 2 Approximately total yield of mass number
 Class 3 Partial yield of mass number

**W. W. Meinke, G. C. Wick, and G. T. Seaborg, University of California Radiation Laboratory Report UCRL-868 (Sept. 26, 1950).

III. ISOBARIC YIELD STUDIES

A. Introduction

As mentioned in the introduction (cf., page 4) identification of the charge of the fissioning nucleus depends upon the determination of the primary fission products. An experimental attempt has been made here to measure the independent yields of various members of each of several reference mass chains. The nuclide whose yield corresponds to the maximum of the curve obtained by plotting the independent yield as a function of atomic number for a given mass number is defined to be the primary product for that mass number. In practice it is usually quite difficult experimentally to measure directly the independent yields for all of the members of a given mass chain. Those independent yields which have been measured experimentally are listed in Table II below. The yields of the measured members furthest from stability for any chain include the yields of their precursors, except in the case of a shielded nuclide.

B. Experimental Techniques

Of the several techniques used in measuring independent yields, the choice depends upon the half-lives and the relative difficulty of the separation chemistry for the species sought. For example, consider the chain of mass 111:

The uranyl nitrate target was bombarded for 2.0 minutes, fused, poured into a dissolver solution containing a known quantity of silver carrier

and some palladium "holdback" agent, and the solution divided into two portions. From one portion, silver chloride was immediately precipitated to separate from palladium.

Table II
Independent and Isobaric Yield Data

Mass Number	Nuclide Measured	Relative Yield	Estimated Fraction of Total Chain
76	As ⁷⁶	0.009	0.05
83	Se ⁸³	0.22 +	0.6
86	Rb ⁸⁶	0.59	0.6
111	Pd ¹¹¹	1.76	0.5
	Ag ¹¹¹	0.44	0.12
136	Cs ¹³⁶	0.25	0.12
140	Ba ¹⁴⁰	1.00	0.43
	La ¹⁴⁰	0.48	0.21
	Nd ¹⁴⁰	0.18	0.075
166	Dy ¹⁶⁶	0.0019	0.044
	Ho ¹⁶⁶	0.0020	0.047
	Yb ¹⁶⁶	0.030	0.72

This separation was accomplished within three minutes after the end of the bombardment. The other portion was allowed to stand until the 26 minute Pd¹¹¹ had all decayed to Ag¹¹¹. [The silver fractions were then purified separately. From the initial specific activity of the silver obtained in the two cases and the known half-lives of the two species, it was possible to calculate from the integrated decay equations the independent yield of Ag¹¹¹ and the yield of Pd¹¹¹ plus its precursors. An example of another type of treatment is afforded by the chain of mass 140:

Since the activities involved are relatively long, a one hour bombardment could be used. Separation of the two species was accomplished within one to two hours after bombardment. After purification of the two fractions and counting of the radioactive samples, the observed yield of Ba^{140} was used to correct the La^{140} activity for that portion which had grown from barium during bombardment and before separation of the species. In this way the independent yield of La^{140} was obtained.

In cases where the independent yield of daughter activity is small relative to the parent, precautions must be taken to minimize the amount of contribution from the parent in the initially separated sample of daughter activity. This may be done by reducing the bombardment time, minimizing the time elapsed from end of bombardment to initial separation of the desired activity, and developing a specific separation procedure which is rapid and essentially complete in one operation.

Independent yields of "shielded" nuclides may be measured directly since the activity could not grow from the neighboring isobars which are stable.

C. Interpretation of the Data

In order to interpret the data obtained for independent yields, the assumption is made that the independent yields of the various isobars of a given decay chain are distributed symmetrically about some particular Z in a manner which can be well approximated by the normal curve of error,* using suitable parameters to adjust the half-width and peak

*A similar assumption was used by Glendenin, Coryell, and Edwards²⁶ in the development of their hypothesis of Equal Charge Displacement for primary fission fragments from slow neutron fission of U^{235} and Pu^{239} . However, the approximation proposed above is not dependent upon the Equal Charge Displacement hypothesis (which, from the experimental data, does not appear to hold for the type of fission discussed in this paper).

height of such a distribution curve to the experimental results obtained. A description of the mathematical method of fitting the normal curve of error to such data is given in Appendix II.

It will be seen from Appendix II that three experimental data are necessary and sufficient to establish the constants of the curve. We can therefore obtain some idea of the validity of the basic assumption by studying the independent yields in chains containing more than three members. Potentially suitable chains are those of masses 166, 141, 111, and 72, each chain containing four measurable members.

Initial sets of three experimental data have been obtained for the chains of mass 140 and mass 166. The decay schemes of these chains are shown in Figure 2. Figures 3 and 4 show the standard-curve-of-error histograms for the mass 140 and mass 166 chains, respectively. The parameters for these curves are tabulated in Table III.

Table III
Parameters for Standard Curve of Error for Isobaric Yield Data

	Z_c	Standard Deviation	Z_c/A
mass 140	57	1.9	0.41
mass 166	71	2.7	0.43

It is apparent that if one could predict the parameters of these charge-distribution histograms as functions of the chain mass number, it would be possible to derive correction factors for each mass number to give the total chain yield, including stable nuclides, in terms of

the yield of any nuclide of the chain. The rough estimates of total chain yields given in Table II were made on the basis of the few data presently available.

IV. SPALLATION PRODUCTS

A. Introduction

The work of O'Connor and Seaborg⁴ on the bombardment of uranium with 380 Mev helium ions showed that there was apparently a continuous yield of radioactive products for the entire range of elements from the uranium region down to the vicinity of atomic number 25. Above mass 120 the yield of fission products decreased with increasing mass number. In the region above mass 200 the yield curve was observed to increase with increasing mass. This increase was attributed to products formed by high energy spallation of uranium. The yield of products found in the region of the minimum of the curve might be attributed to a combination of fission and spallation reactions. That fission can occur in such a manner as to give products of such high mass was shown by the observation of complementary product nuclei of low mass.

In the present work it was observed that the primary fission products tend toward the neutron deficient side of stability with increasing mass number as was found for bismuth fission.¹ However, in the region of mass 180 to 200, several β^- emitting nuclides have been observed. These are attributed tentatively to spallation reactions.

B. Results

Hafnium.-- The purified hafnium fraction showed a negative beta activity having an energy of about 0.4 Mev and long life. This activity

has been attributed to Hf^{181} .

Osmium.-- Decay of the osmium fraction showed a component of about 32 hours half-life which was attributed to Os^{193} .

Gold.-- The decay of the gold sample gave indication of the 14 hour and 5.6 day isomers of Au^{196} . An intermediate activity was observed which seemed to be a mixture of Au^{198} and Au^{199} (2.7 day and 3.3 day, respectively). Aluminum absorption measurement on this activity showed a beta energy of about 1 Mev and a softer component whose energy was not determined.

Radium.-- Decay of the radium samples was followed by both Geiger counter measurements and alpha particle counting. From the decay curves and pulse analysis of the alpha activity, radium isotopes of mass 223, 224, and 225 were identified. A new Geiger counter activity, having a half-life of the order one to two hours, was observed in the separated radium fraction. This activity might be from Ra^{227} , Ra^{230} , or a mixture of both.

Actinium.-- The formation of Ac^{226} was indicated by the presence of a short-lived thorium alpha activity eluted from an ion exchange resin column some 20 to 30 hours after bombardment. The activity was identified as thorium by its elution characteristics.

V. DISCUSSION

From examination of the data herein presented, a few marked trends are observed. Almost all of the low mass nuclides identified were of the neutron excess type. As higher mass numbers were approached, neutron deficient nuclides increased in relative abundance of formation.

However, in the spallation region, which merges with the region of heavy fission fragments in the vicinity of mass number 180, neutron-excess nuclides again predominate.

Let us consider a nuclide formed by high energy spallation of a U^{238} nucleus, this nuclide having an amount of internal energy much in excess of the fission threshold. This energy may be dissipated in one of three different ways: it may in part be used to cause fission, any excess being carried off by the fission fragments, by particle emission, or by radiation; it may be dissipated as radiation, the nuclide in question descending to a nonfissioning ground state; or it may be carried off, in part or entirely, by an emitted nucleon or composite particle, such as an alpha particle or a deuteron, leading to a different nuclide which again may undergo one of these three changes. The mechanism involved probably compares more closely to the case for "fast fission" of bismuth¹ than to the so-called "slow fission" of U^{235} induced by thermal neutrons.

If we represent all the possible nuclides as points on a plane with coordinate axes Z and $A-Z$, then the various spallation and fission products possible from U^{238} with protons will all fall within that portion of the first quadrant of this plane having $Z \leq 93$, $A-Z \leq 146$. Normalizing the total probability of fission to unity, the various partial fission probabilities of the nuclei lying within the fissioning region can be described by a contour map. The contour lines are the loci of points of equal partial fission probability. The fission product yield curve may be plotted in a similar manner on the same

Figure 1 (cont. Figure 2)

chart (see Figure 5).^{*} The dotted lines of slope -1 represent isobaric chains. The independent yield of the members of these chains as a function of Z is given by the value of the contour line intersected for each Z .

The contour representation of fission product yields offers a criterion for establishing the charge to mass ratio of the primary fission products. If the charge to mass ratio is constant, as in the case for bismuth fission,¹ the curve connecting the points of maximum relative yield for a given mass number (i.e., the so-called "ridge line") will be a straight line. Although the present data are not conclusive, there is a definite suggestion (cf. Figure 5) that the "ridge line" is not straight, i.e., Z/A is not constant for the fission products. (Analysis of the isobaric charge distribution curves, cf. Section III, indicates the same result.) If this phenomenon is real, one would expect a distribution of fissioning nuclei rather than a single dominant fissioning species.

We may assume that the shape of the fissioning-nucleus contour map is markedly energy-sensitive. Let us further assume that the fission-fragment yield distribution is uniquely determined by the fissioning-nucleus distribution. Some qualitative predictions of the behavior of the fission-fragment yield curve with variation of bombarding energy may then be made.

The most obvious effect of increasing the bombardment energy will be to increase the number of intermediate spallation products leading

^{*}In the figure, the bombardment product fission probability contours (upper right corner of Figure 5) are hypothetical; the fission product yield contours are expressed relative to Ba^{140} (including its precursors) = 1.0.

to fission, since Douthett⁸ has shown that excess bombarding energy does not appear as kinetic energy of the fragments. This will lead to a lower average mass for the "fissioning nucleus," with its concurrent effect of lowering the mass of the fission fragments which have the maximum yield. Also, should neutrons be evaporated from the excited nuclides in preference to protons or other charged particles, as seems likely, the charge-to-mass ratio of the average fissioning nucleus, and hence of its fragments, should be increased. It is thus expected that at high energies the nuclides closer to stability, or even on the neutron deficient side, should appear in greater relative abundance, as is actually observed.

The formation of Cu^{61} (neutron deficient) and Cu^{64} (shielded) as fission products with yield of the order of magnitude of Cu^{67} , in the region where the formation of neutron excess nuclides is expected to predominate, suggests that there is an effective mode of fission differing from the simple symmetric binary fission discussed above. If a large number of neutrons were evaporated from the excited target nucleus, an energetically favorable ternary fission mechanism could lead to the observed copper isotopes. The high yield of Na^{24} relative to the extrapolated smooth curve (Figure 1) may also point in this direction.

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APPENDIX I

General Chemical Procedures*

Sodium.-- The uranium target was dissolved in nitric acid containing a known amount of sodium ion as carrier. The uranium was extracted into a solution of tributyl phosphate in benzene. After boiling the aqueous phase to reduce its volume, strontium and barium nitrates (carrying radium) were precipitated from fuming nitric acid. The excess nitric acid was removed and silver chloride and manganese dioxide precipitated. The supernatant was boiled to dryness with hydrochloric acid. The residue was taken up in water and barium sulfate precipitated. From the supernatant, sodium zinc uranyl acetate was precipitated. This precipitate was dissolved in 6 N hydrochloric acid and sodium chloride precipitated from isopropyl alcohol saturated with hydrogen chloride gas. The precipitate was dissolved in 0.2 N hydrochloric acid and the members of the acid sulfide group precipitated by passing in hydrogen sulfide gas. The solution was made alkaline with ammonium hydroxide and hydroxides and sulfides precipitated. The supernatant was evaporated to near dryness and the residue taken up in 0.2 N hydrochloric acid. Sodium zinc uranyl acetate was precipitated and then sodium chloride as above. This precipitate was taken up in perchloric acid, potassium, rubidium, cesium and ruthenium carriers added, and the solution fumed to small volume. The solution was chilled and isopropyl alcohol added. After centrifuging and discarding the insoluble perchlorates, the supernatant was saturated with hydrogen chloride gas

* Many of these procedures are modifications of procedures developed on the Plutonium Project²⁷ and by the chemistry group of the Radiation Laboratory at Berkeley.²⁸

while kept at ice temperature to precipitate sodium chloride. The sodium chloride was reprecipitated, washed, dried at 110°C , and sodium determined by weighing as NaCl.

Manganese.-- From a nitric acid solution of the uranium target containing manganese carrier, manganese dioxide was precipitated by the addition of potassium bromate. The precipitate was dissolved in dilute nitric acid containing hydrogen peroxide. Concentrated nitric acid was added and the manganese oxidized to permanganate by the addition of sodium bismuthate. After centrifuging to bring down the excess bismuthate (insoluble), the supernatant was decanted and the permanganate reduced by the addition of oxalic acid. Silver chloride was precipitated to remove any acid insoluble compounds not brought down on the excess sodium bismuthate. The supernatant was diluted and members of the acid sulfide group were precipitated by the addition of hydrogen sulfide gas. The supernatant was made basic and manganous sulfide precipitated. The sulfide was dissolved in nitric acid and the foregoing procedure repeated for additional purification. After dissolving the sulfide from this second cycle, manganese dioxide was precipitated and the manganese determined by weighing as Mn_3O_4 after ignition.

Iron.-- Iron carrier in an aqua regia solution of the target (containing the minimum amount of nitric acid) was boiled with concentrated hydrochloric acid to remove most of the nitrate. The material was taken up in 9 N hydrochloric acid and the iron extracted into di-isopropyl ether. After thoroughly washing the ether layer with

7.5 N hydrochloric acid, the iron was re-extracted into water.* The aqueous solution was acidified to 1 N hydrochloric acid and antimony and tellurium sulfides precipitated. Ferric hydroxide was precipitated with ammonia gas using barium and strontium "holdback" agents. The precipitate was dissolved in hydrochloric acid, ruthenium carrier added, and the solution fumed with perchloric acid. Ferric hydroxide was reprecipitated with ammonia and dissolved in nitric acid. Niobium oxalate complex was added and niobium pentoxide precipitated. Barium sulfate and silver iodide were also precipitated to remove radioactive impurities. Ferric hydroxide was reprecipitated with ammonia and dissolved in 3 N nitric acid. Hydrofluoric acid was added and barium fluozirconate precipitated. Ferric hydroxide was precipitated from the supernatant and dissolved in 9 N hydrochloric acid for extraction with di-isopropyl ether. Upon re-extraction into water, the iron was precipitated with ammonia. The hydroxide was washed and ignited, and the iron determined by weighing as Fe_2O_3 .

Cobalt.--- The acidic target solution containing cobalt carrier was made strongly ammoniacal. The supernatant was removed and the precipitate washed twice with hot aqueous ammonia. From the combined supernatant and washings, ferric hydroxide and barium and strontium carbonates were precipitated. The supernatant was acidified with hydrochloric acid and the acid sulfide group contaminants removed by precipitation with hydrogen sulfide gas. The solution was made basic and cobalt sulfide precipitated. The sulfide was dissolved in

*It was recently found that the yield of iron was materially increased by re-extraction into an acetic acid-sodium acetate buffer solution instead of into water.

concentrated nitric acid which was then diluted for precipitation of silver chloride. The supernatant was made basic with potassium hydroxide to precipitate cobalt hydroxide. This was dissolved in 2 to 3 N acetic acid. Nickel "holdback" agent was added and potassium cobaltinitrite precipitated. The precipitate was dissolved in concentrated hydrochloric acid and the procedure repeated beginning with the ferric hydroxide - alkaline earth carbonate precipitations. The second cobaltinitrite precipitate was dissolved as before and potassium cobaltinitrite reprecipitated. This final precipitate was washed, dried at 110°C and cobalt determined by weighing as $K_3Co(NO_2)_6 \cdot H_2O$.

Nickel.-- The acidic target solution containing nickel carrier was made strongly ammoniacal. The supernatant was removed and the precipitate washed twice with hot aqueous ammonia. From the combined supernatant and washings, ferric hydroxide and barium and strontium carbonates were precipitated. The solution was boiled gently to remove some of the excess ammonia, and dimethylglyoxime added to precipitate the nickel. The precipitate was dissolved in concentrated nitric acid which was then diluted to approximately 1 N. Copper, palladium, and antimony sulfides were precipitated several times. The supernatant was boiled to remove excess hydrogen sulfide, then made basic with ammonia gas. Ferric hydroxide was precipitated again. The supernatant was made 0.5 N in hydrochloric acid and palladium dimethylglyoxime was precipitated. The supernatant was neutralized and nickel dimethylglyoxime precipitated. After reprecipitation and washing, the nickel dimethylglyoxime was dried at 110°C and weighed as such.

Copper.-- The acidic target solution containing copper carrier was made strongly ammoniacal. The supernatant was removed and the precipitate washed twice with hot aqueous ammonia. From the combined supernatant and washings, ferric hydroxide was precipitated. A 5 percent solution of sodium thiocyanate and sodium sulfite was added to the supernatant and it was acidified with glacial acetic acid, after "holdback" agents of the ammonia complex group elements had been added. The cuprous thiocyanate precipitate was dissolved in a minimum amount of concentrated nitric acid and the solution made 2 N in hydrochloric acid. Cadmium, yttrium, and strontium "holdback" agents were added, and copper precipitated as the sulfide. The cupric sulfide was dissolved in concentrated nitric acid which was diluted to approximately 4 N for the precipitation of silver chloride. The supernatant was buffered with ammonium hydroxide - sodium acetate, and copper thiocyanate again precipitated. The precipitate was washed, dried at 110°C, and copper determined by weighing as CuCNS.

Zinc.-- The nitric acid solution of the target containing zinc carrier was diluted to approximately 1 N and zinc mercurithiocyanate precipitated in the presence of oxalic acid. The precipitate was dissolved in 4 N nitric acid, the solution was diluted and the zinc mercurithiocyanate reprecipitated twice. The precipitate was redissolved, the solution diluted, and copper, silver, tin, antimony, and bismuth sulfides precipitated. The supernatant was buffered with ammonium acetate, and zinc sulfide precipitated. The precipitate was dissolved in concentrated hydrobromic acid and evaporated to dryness several times with bromine-hydrobromic acid to remove selenium. The residue

was taken up in 1 N sodium hydroxide to which sodium carbonate had been added. Ferric hydroxide and barium and strontium carbonates were precipitated from this solution. The supernatant was acidified to 1 N in hydrochloric acid. Zinc mercuric thiocyanate was precipitated, washed, dried at 110°C and weighed as such. The gravimetric factor was determined empirically. [N.B. A better sample for counting purposes may be obtained by dissolving the final zinc mercurithiocyanate precipitate, removing the mercury by precipitating it as mercuric sulfide, neutralizing to methyl orange endpoint, and precipitating zinc ammonium phosphate at about 80°C.²⁹ The precipitate is dried at 105°C and weighed as $\text{Zn}(\text{NH}_4)\text{PO}_4$.]

Arsenic.-- The nitric acid solution of the target containing arsenic carrier was boiled nearly to dryness. (N.B. A more recent method removes the nitrate by boiling with formic acid.)³⁰ The residue was taken up in 6 N hydrochloric acid, a crystal of ammonium iodide added, and arsenic and germanium sulfides precipitated at ice temperature. The sulfides were washed with 6 N sulfuric acid saturated with hydrogen sulfide. The sulfides were dissolved in concentrated ammonium hydroxide. The solution was washed into a glass still, and tellurium, antimony and tin "holdback" agents added. Concentrated hydrochloric acid was added and germanium tetrachloride was distilled from the solution in a stream of chlorine gas. Hydrogen chloride gas was passed into the residue to remove the chlorine. Cuprous chloride was added to reduce the arsenic to arsenic(III), and arsenic trichloride was distilled from the solution in a stream of hydrogen chloride. The arsenic trichloride was trapped in concentrated hydrochloric acid at

ice temperature. Arsenic(III) sulfide was precipitated from the distillate by the addition of hydrogen sulfide gas. The sulfide was dissolved in concentrated ammonium hydroxide, tellurium, antimony, and tin carriers added, and the arsenic trichloride distilled from hydrochloric acid as above. Arsenic(III) sulfide was again precipitated from the distillate and dissolved in concentrated ammonium hydroxide. The solution was acidified with concentrated hydrochloric acid and arsenic(III) sulfide precipitated with hydrogen sulfide. The precipitate was washed, dried at 110°C , and arsenic determined by weighing as As_2S_3 .

Selenium.-- The uranium target was dissolved under reflux in hydrobromic acid containing bromine, and selenium and tellurium carriers. After solution was complete, the reflux column was replaced by a still head and selenium tetrabromide distilled into bromine water kept at ice temperature. After completion of the distillation, an equal volume of concentrated hydrochloric acid was added to the bromine water at ice temperature, and sodium bisulfite added to reduce the selenium to the red allotropic modification of the zero oxidation state. After washing, the selenium was dissolved in hydrobromic acid containing bromine and tellurium "holdback" agent, and redistilled. The reduction and distillation were repeated. The selenium from the final reduction was washed with water and dried with ethanol and diethyl ether. The precipitate was then dried at 110°C and selenium determined by weighing as Se.

Bromine.-- The uranium target was dissolved under reflux in nitric acid containing a known amount of freshly precipitated silver bromide

(to prevent loss of bromine by volatilization). Exchange of the radioactive bromine or bromide ions with the inert bromide of silver bromide is presumed to be rapid and complete.³¹ After separation from the target solution, the silver bromide was washed well and metathesized to silver sulfide in ammoniacal solution. The supernatant was carefully acidified to 1 N in nitric acid, allowing the excess hydrogen sulfide to escape. Iodide carrier was added, oxidized to iodine with 0.1 M sodium nitrite, and extracted into carbon tetrachloride. The iodine extraction was repeated twice. The bromide was then oxidized to bromine by potassium permanganate and extracted into carbon tetrachloride. The organic phase was washed with 1 N nitric acid containing permanganate. The carbon tetrachloride was stirred with water and sodium bisulfite solution added until the bromine had been reduced to bromide (and consequently gone into the aqueous phase). The bromide was then precipitated by the addition of silver nitrate, washed, dried at 110°C, and weighed as AgBr.

Rubidium.-- An aliquot of the nitric acid solution of the target containing cesium and rubidium carriers was evaporated to fuming with perchloric acid. After cooling, absolute ethanol was added and the solution stirred at ice temperature. The cesium and rubidium perchlorates were washed with absolute ethanol and dissolved in 0.2 N hydrochloric acid. Silver chloride was precipitated, then tellurium, ruthenium, tin, antimony, and silver sulfides. The solution was made basic with sodium hydroxide, and lanthanum, cerium, yttrium, iron, zirconium, and niobium precipitated. Barium and strontium carbonates were then precipitated. The series of sulfide, hydroxide and carbonate

precipitations was repeated several times. The final supernatant was evaporated to fuming with perchloric acid. The perchlorates were washed with absolute ethanol, dissolved, and reprecipitated. The perchlorates were then dissolved in 6 N hydrochloric acid and the cesium precipitated with silicowolframic acid. (For further purification of cesium see below.) More cesium carrier was added to the supernatant and cesium silicowolframate again precipitated. The supernatant was evaporated to near dryness. Chloroplatinic acid and ethanol were added to precipitate rubidium chloroplatinate. The precipitate was washed with ethanol, dried at 110°C and rubidium determined by weighing as Rb_2PtCl_6 .

Strontium.-- The target was dissolved in a minimum volume of concentrated nitric acid containing carriers of the elements to be isolated. After solution was complete, red fuming nitric acid was added and the tube chilled in an ice bath. The precipitate, containing the nitrates of strontium, barium, and coprecipitated radium, was centrifuged and the supernatant decanted. The nitrates were dissolved in a minimum amount of warm water and reprecipitated with fuming nitric acid. The nitrates were redissolved and the solution made 4 N in nitric acid. Silver chloride was precipitated to remove acid insoluble materials which might have been carried by the alkaline earth nitrates. The supernatant was made basic with ammonia gas and ferric hydroxide precipitated to remove traces of ammonium hydroxide group impurities and any insoluble material which might have remained in the solution. The supernatant was buffered to pH 5 with acetic acid - ammonium acetate. Barium chromate (carrying radium) was separated from the strontium

by precipitation at 95°C. Barium chromate was again precipitated from the supernatant in order to remove any traces of radioactive barium or radium. Strontium was precipitated as the carbonate, washed, dissolved in hydrochloric acid to remove carbon dioxide and reprecipitated as the oxalate for weighing.

Zirconium.— The nitric acid solution of the target containing zirconium carrier was made about 4-5 N in nitric acid and about 8 N in hydrofluoric acid. Lanthanum and yttrium fluorides were precipitated twice to remove contaminants of the rare earth and actinide series. Barium was added to the supernatant to precipitate barium fluozirconate. The precipitate was dissolved in 8 N nitric acid saturated with boric acid. The foregoing precipitations were repeated for additional purification. The final BaZrF_6 precipitate was dissolved in approximately 3 N hydrochloric acid with boric acid added to complex the fluoride. The barium was removed by precipitation as barium sulfate. The supernatant was diluted to approximately 2 N in acid and the zirconium precipitated by 6 percent cupferron solution in the cold (ice bath). The precipitate was washed with the reagent, transferred to a porcelain crucible, ignited and weighed as ZrO_2 . This procedure probably effects no separation from hafnium. However, the yield of hafnium isotopes is less than 10^{-3} that of the zirconium.

Niobium.— Niobium carrier, complexed with oxalate, was added to a measured fraction of the target solution. Niobium pentoxide was precipitated by digesting in an 8 N nitric acid solution containing potassium bromate. The oxide was dissolved in saturated oxalic acid. The solution was taken up in 6 N hydrochloric acid and extracted with cupferron into

chloroform at 5°C. The aqueous phase was re-extracted and the combined chloroform layers washed with cold 6 N hydrochloric acid containing cupferron. The chloroform layer was boiled with concentrated nitric acid and potassium bromate added to precipitate niobium pentoxide. The oxide was dissolved in dilute nitric acid containing hydrofluoric acid. Barium fluozirconate precipitated to remove zirconium, yttrium, and lanthanide contaminants. Boric acid was added to complex the fluoride, and niobium pentoxide was precipitated from strongly ammoniacal solution. After washing, the oxide was dissolved in saturated oxalic acid, then reprecipitated from 8 N nitric acid containing potassium bromate. After washing, the precipitate was ignited and weighed as Nb_2O_5 .

Molybdenum.-- The uranium target was dissolved in hydrochloric acid containing molybdenum carrier and the solution completed by the addition of minimum amounts of nitric acid. The solution was boiled to reduce the amount of nitrate and bring the concentration of hydrochloric acid to about 6 N. Molybdenum was extracted with several portions of diethyl ether. (A minimum amount of liquid bromine was added to the aqueous phase to ensure that molybdenum was present in the VI oxidation state.) The ether layers were combined, washed with 6 N hydrochloric acid, and evaporated over water. Ferric ion and niobium oxalate complex were added to the solution, and their hydrated oxides precipitated by addition of ammonia. The supernatant (containing molybdenum as molybdate) was acidified to about 0.5 N in hydrochloric acid. Molybdenum alpha-benzoin oxime was precipitated from the chilled solution. After washing with 0.5 N sulfuric acid, the oxime was dissolved in concentrated nitric acid and destroyed by boiling carefully to fuming with perchloric acid.

After the solution had been cooled and diluted, ferric hydroxide was precipitated using sodium hydroxide. The supernatant was acidified and molybdenum alpha-benzoin oxime reprecipitated and destroyed. After another precipitation of ferric hydroxide, the supernatant was made just acid and buffered with sodium acetate. Molybdenum was precipitated as silver molybdate, washed, dried at 110°C and weighed as Ag_2MoO_4 .

Ruthenium.-- Ruthenium and osmium carriers were added to the nitric acid solution of the target which was then boiled to remove osmium tetroxide. Iodide carrier was added and oxidized with bismuthate to prevent distillation of iodine. Molybdenum was added and complexed with phosphate to prevent distillation of molybdenum. Ruthenium tetroxide was then distilled from fuming perchloric acid in an air stream. To the distillate, trapped in 6 N sodium hydroxide, ethanol was added and the solution boiled to coagulate ruthenium oxide. This may be reoxidized to the higher state and distilled from perchloric acid again for additional purification. The oxide recovered from the alcoholic sodium hydroxide was dissolved in hot 6 N hydrochloric acid. The solution was diluted and the ruthenium reduced to the metallic state with magnesium. The ruthenium was washed, dried at 110°C and weighed as the metal.

Palladium.-- The target solution containing palladium carrier was made about 0.4 N in nitric or hydrochloric acid. Inactive nickel was added as a "holdback" agent. The palladium was precipitated with dimethylglyoxime and the precipitate washed with dilute acid (0.2 N). The palladium dimethylglyoxime was dissolved in concentrated nitric acid (destroying the dimethylglyoxime), the solution diluted, and ferric hydroxide precipitated twice with ammonia. Silver iodide was precipitated

twice (using excess iodide) and the solution reacidified to 0.4 N in hydrochloric acid. After centrifuging out any silver chloride which might have been present, the palladium was precipitated with dimethylglyoxime. The procedure could be repeated for additional purification. After washing, the final palladium dimethylglyoxime precipitate was dried at 110°C and weighed as Pd-dmg.

Silver.-- The target was dissolved in nitric acid containing silver carrier (to avoid adsorption of trace amounts of silver by the glass). The solution was diluted to approximately 4 N in nitric acid and silver chloride precipitated from a boiling solution with stirring. Coagulation is rapid and complete under these conditions. The silver chloride was dissolved in aqueous ammonia and ferric hydroxide was precipitated to remove ammonium hydroxide group contaminants. The silver was recovered by precipitation as silver sulfide. The sulfide was dissolved in concentrated nitric acid which was boiled, then diluted to approximately 4 N for precipitation of silver chloride. The cycle was repeated for additional purification. After dissolving the final precipitate of silver sulfide, the solution was diluted and made basic with ammonia. Ferric hydroxide was precipitated to remove any sulfur which might have been present. The supernatant was made approximately 4 N in nitric acid and silver chloride precipitated. After washing and drying at 110°C, silver was determined by weighing as silver chloride. All silver chloride precipitations except the final one should be made in the presence of palladium and cadmium "holdback" agents to minimize occlusion of radioactive contaminants on the surface of the silver chloride.

Cadmium.-- The target solution containing cadmium carrier and copper was made basic with ammonia. Cadmium and copper were leached out of the massive precipitate by hot aqueous ammonia. The completeness of the extraction was indicated by the blue color of the cupri-ammonium complex. Iron, lanthanum, and indium were precipitated from the ammoniacal solution. Cadmium and copper sulfides, precipitated from the supernatant, were dissolved in concentrated nitric acid. The solution was diluted to approximately 4 N and silver chloride precipitated. The supernatant was neutralized with ammonia; enough solid potassium cyanide added to complex copper; and cadmium sulfide precipitated with hydrogen sulfide. The cadmium sulfide was dissolved in 6 N hydrochloric acid, the solution diluted to 2 N, and palladium sulfide precipitated from the hot solution. Antimony sulfide was precipitated from the supernatant. After centrifugation and decantation, the supernatant was made basic with ammonia and cadmium sulfide precipitated. The precipitate was washed, dried at 110°C, and cadmium determined by weighing as CdS.

Tin.-- The target was dissolved in hydrochloric acid containing tin carrier. A minimum amount of nitric acid was used to complete the solution of the uranium. A portion of the target solution was taken and diluted to approximately 1 N in acid. Stannic sulfide was precipitated from the hot solution. After washing, the sulfide was dissolved in concentrated hydrochloric acid and the hydrogen sulfide boiled out. The solution was diluted to 2-2.5 N and antimony sulfide precipitated from the hot solution. The acidity of the supernatant was reduced by the addition of ammonium hydroxide, and stannic sulfide again precipitated. After dissolving the sulfide in hydrochloric acid and boiling out hydrogen

sulfide, the solution was diluted and ruthenium, zirconium, niobium, cadmium and iron carriers added. The solution was made basic with excess 6 N sodium hydroxide. Iron was added to the supernatant and the hydroxide again precipitated. The supernatant was acidified and tin precipitated with hydrogen sulfide. The sulfide was dissolved in hydrochloric acid and antimony sulfide reprecipitated. After the tin sulfide was recovered from the supernatant, it was dissolved in nitric acid and metastannic acid precipitated by the addition of solid ammonium nitrate. The precipitate was filtered, ignited, and weighed as SnO_2 .

A modification to this procedure has been suggested by McDonell.³² The antimony was removed by reduction to metallic antimony with iron. The solution was filtered through "fine" grade sintered glass funnels. Tin was recovered by precipitation of the sulfide from the filtrate. In the sodium hydroxide precipitation of possible contaminants, ammonium polysulfide was added to remove certain elements, such as lead, which would otherwise be soluble in the basic solution. The final precipitate of stannic sulfide was dissolved in ammonium nitrate solution with small amounts of 6 N nitric acid (instead of in concentrated nitric acid) to minimize the amount of sulfur formed.

Tellurium.— The target was dissolved in hydrochloric acid containing tellurium carrier with the minimum amount of nitric acid necessary to complete solution. A portion of the target solution, to which selenium carrier has been added, was boiled to near dryness with concentrated hydrobromic acid two or three times. The residue was taken up in concentrated hydrochloric acid, selenium carrier added, and the red allotropic modification of selenium precipitated by the addition of sulfur

dioxide to the solution at 5°C. The supernatant was diluted to approximately 3 N in hydrochloric acid and tellurium was precipitated by the addition of sulfur dioxide. The tellurium was dissolved in a few drops of concentrated nitric acid, the excess nitric acid evaporated, and the solution diluted. 6 N sodium hydroxide was added dropwise until the precipitate of tellurous acid which formed was thoroughly dissolved. Ferric hydroxide was precipitated from this solution. Tellurium was recovered by precipitation with sulfur dioxide from the acidified supernatant. The procedure was repeated for additional purification. The final tellurium precipitate was washed, dried at 110°C, and weighed as Te.

Cesium.— (See rubidium procedure, page 46.) The cesium and rubidium perchlorates were taken up in 6 N hydrochloric acid and cesium precipitated with silicowolframic acid. After digestion at 95°C, the solution was chilled and centrifuged. The precipitate was washed with 6 N hydrochloric acid and dissolved in dilute sodium hydroxide. Upon reacidification, wolframic oxide and silica precipitated. Inert rubidium was added as a "holdback" agent, and the cesium reprecipitated with silicowolframic acid. The precipitate was dissolved and cesium reprecipitated as before. The precipitate was washed with 6 N hydrochloric acid, dried at 110°C and the cesium determined by weighing as $\text{Cs}_8\text{SiW}_{12}\text{O}_{42}$.

Barium.— (See strontium procedure, page 47.) The barium chromate separated from the strontium was washed with water at 95°C. The precipitate was dissolved in a minimum amount of hot 6 N hydrochloric acid. The solution was taken up in ether-concentrated hydrochloric acid, 1:5 by volume, the "ether-HCl reagent." Upon chilling at ice temperature, the barium chloride precipitated. The chloride was dissolved

in a minimum amount of distilled water and reprecipitated twice. The final precipitate was washed with absolute alcohol and with ether, and dried in a vacuum desiccator. The barium was determined by weighing as $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

Hafnium.-- Hafnium and zirconium were separated together from other fission products by the above described procedure for zirconium. Hafnium was separated from zirconium by elution from cation exchange resin with constant boiling hydrochloric acid.³³ Since the hafnium is eluted first, tailing from the higher activity zirconium peak does not interfere.

Osmium.-- After carefully dissolving the uranium target in nitric acid under reflux, carrier osmium having previously been added to the nitric acid, iodine and bromine "holdback" agents were added, oxidized with sodium bismuthate, and osmium tetroxide distilled into 6 N sodium hydroxide. Hydrogen sulfide gas was passed in to precipitate osmium sulfide. After washing, the sulfide was dissolved in concentrated nitric acid, and the distillation-precipitation cycle repeated twice. The sulfide precipitate was then dissolved in perchloric acid. Molybdenum "holdback" agent was added and complexed with phosphate. Osmium tetroxide was distilled from this solution. After precipitation of the sulfide, the perchloric acid distillation was repeated. The solution of osmium in 6 N sodium hydroxide was carefully acidified with hydrochloric acid and the osmium(VIII) reduced with magnesium to metallic osmium.

Gold.-- Gold was separated as the metal by a series of precipitations from chloride-free nitric acid solution with sulfur dioxide in

the presence of mercury, tellurium, and platinum "holdback" agents. The gold was then dissolved in a minimum of aqua regia and taken up in 2 N hydrochloric acid from which it was extracted by ethyl acetate. Gold was recovered by evaporating the organic layer over dilute nitric acid and precipitating metallic gold with sulfur dioxide.

Radium.-- (See barium procedure, page 54.) The final precipitate of barium chloride was washed with alcohol to remove any excess hydrochloric acid. The precipitate was then dissolved in water and equilibrated with Dowex-50 cation exchange resin. By elution through a column packed with resin, using pH 8 ammonium citrate solution, the barium and radium fractions were separated.³⁴ Samples for alpha counting were mounted on platinum disks and flamed to destroy and remove citrate, leaving essentially weightless samples.

General Procedure for Isolating and Separating Rare Earths*

General.-- One milligram of each rare earth to be isolated (except promethium, for which tracer was added) was added as carrier, the total amount being of the order of twelve milligrams. The group was separated by precipitation of the fluorides from 2 N nitric acid solution by addition of hydrofluoric acid. (Some uranyl fluoride may be carried if the concentration of uranium is high enough. For one of the bombardments which used an eight gram uranium target, the uranium was extracted with ether from the nitric acid solution before the rare earth fluorides were precipitated.) The fluorides were dissolved in 8 N nitric acid saturated with boric acid, and the rare earths

*Modification of a procedure used by Wilkinson and Hicks.²⁵

were recovered as hydroxides by precipitation with ammonia gas. The hydroxides were washed to remove excess ammonium salts, and dissolved in dilute hydrochloric acid. Selected sulfides (copper, arsenic, antimony, tin, silver, palladium, bismuth) were precipitated from this solution by addition of hydrogen sulfide gas to remove contaminants belonging to the acid sulfide group. From a hydrochloric acid concentration of the order 0.3 N, the rare earths were then precipitated as oxalates. After washing, the oxalates were dissolved in concentrated nitric acid containing potassium bromate. The solution was diluted and the rare earth hydroxides reprecipitated. The hydroxides were dissolved in 0.2 N hydrochloric acid which was then diluted to between pH 1 and pH 2. The solution was equilibrated with Dowex-50 ion exchange resin for five minutes at 95°C.

Cerium.-- In addition to separation by the general procedure, cerium has also been separated from the other rare earths by oxidation to cerium(IV) and precipitation of ceric iodate. Ceric phosphate precipitations have also been used to separate cerium from the other rare earths.

Europium.-- Europium was separated from the other rare earths by reduction to europium(II) with zinc amalgam in a nitrogen atmosphere. The other rare earths were precipitated as hydroxides from a carbonate free solution leaving the europium(II) in solution. The europium was recovered by ozone oxidation to europium(III) and hydroxide or oxalate precipitation. The cycle may be repeated for additional purification.

Column Separations

The resin, with adsorbed rare earths, was placed in a band at the top of a glass column 4 mm in diameter and 10 cm high, previously packed with Dowex-50 resin, and eluted with constant boiling (~6 N) hydrochloric acid at a temperature of 87°C, using a flow rate of approximately 0.1 ml per minute. After about two hours, the rare earths from lutetium through neodymium had been eluted, leaving behind about 30 percent of the praseodymium, 50 percent of the cerium, 60 percent of the lanthanum and all of the actinium with its thorium daughter activities. The rare earths were recovered from the 6 N hydrochloric acid solution by precipitation of the hydroxides with ammonia gas. The hydroxides were washed, dissolved, and equilibrated with resin as before. The resin was then placed at the top of a glass column 7 mm in diameter and 20 cm high, previously packed with resin, and eluted with 0.25 M ammonium citrate-citric acid solutions at 87°C. Lutetium and ytterbium were separated by elution with pH 3.19 citrate at a flow rate of 0.14 ml per minute. Ytterbium, thulium, erbium, and holmium were separated by elution with pH 3.23 citrate at a flow rate of 0.21 ml per minute. For the lighter rare earths, pH 3.30 and pH 3.5 citrate solutions were used successively. Dysprosium-yttrium and europium-gadolinium were not separated under these conditions. The dysprosium-yttrium separation was made by elution with pH 3.05 citrate on another resin-packed column at room temperature.

Recovery and Chemical Yield

By means of a turntable actuated by a microflex timer, samples of the elutriant were collected at regular intervals. Small aliquots of these samples were mounted on counting plates for radioassay. From the plot of relative activity versus sample number it was possible to identify the various peaks representing the separated rare earths. Identification of the peaks was made more definite by spectrographic analysis.

From the radioassay plot it was possible to select the samples comprising a given peak which were free from any contamination by the material comprising neighboring peaks. These samples were combined in a small erlenmeyer flask and fumed with sulfuric acid to which a few drops of selenium(IV) solution were added as a catalyst. The destruction of the citrate was completed by adding perchloric acid and heating. The rare earth was recovered by precipitation as the hydroxide. After washing out the ammonium perchlorate, the hydroxide was dissolved and the oxalate precipitated. The oxalate was dried in a vacuum desiccator at room temperature, and weighed to determine the percentage recovery of the rare earth. (The oxalate was selected for the gravimetric analysis because of the high molecular weight of its stable hydrate. In this way small amounts of a rare earth could be determined with greater accuracy since there are two to three grams of the compound per gram of rare earth.)

APPENDIX II

Let us consider data which are of the following form: (1) the total yield of isobars of charge $Z-1$ or less; (2) the independent yield of the isobar of charge Z ; and (3) the total yield of isobars of charge $Z + n + 1$ or greater, where n is the number of isobars not available for chemical separation, i.e., stable or short lived isobars. Let the area under the histogram be equal to unity. Now let us define a function $E(X)$ such that:

$$E(X) = \int_X^{+\infty} f(Z)dZ \quad (\text{AII-1})$$

X being the abscissa with the center of the curve taken as the origin, X being expressed in units of the standard deviation of the curve. Then if we define y as shown in Figure 6 (taking y as a positive number when in the direction shown), and the width of one block of the histogram (in X units) is a , the experimental data may be described as proportional to $E(y)$, $E(y-a) - E(y)$, and $E(b)$.

Figure 7 gives $E(y)/E(y-a)$ as a function of y for various values of a . From the experimental value for $E(y)/E(y-a)$ one obtains from this chart a table giving y as a function of a .

Now

$$|b| = (n+1)a - |y|, \quad (\text{AII-2})$$

so we have

$$y = f_1(a) \quad (\text{AII-3})$$

and

$$b = f_2(a) \quad (\text{AII-4})$$

therefore

$$E(y) = f_3(a) \quad (\text{AII-5})$$

$$E(b) = f_4(a) \quad (\text{AII-6})$$

therefore

$$E(b)/E(y) = f_5(a) \quad (\text{AII-7})$$

where $E(b)/E(y)$ can be obtained from the experimental data. Equation (AII-7), of the form $f_5(a) = \text{constant}$, can then be solved by graphical means, giving a value for a , hence for y , and hence locating Z_0 the center of the curve as

$$Z_0 = Z - 1/2 + y/a . \quad (\text{AII-8})$$

Since a histogram block has a width of 1 charge unit and a standard-deviation units, the standard deviation of the curve is $1/a$.

REFERENCES

1. R. H. Goeckermann and I. Perlman, Phys. Rev. 73, 1127 (1948), and Phys. Rev. 76, 628 (1949).
2. A. S. Newton, Phys. Rev. 75, 17 (1949).
3. J. Jungerman and S. C. Wright, Phys. Rev. 76, 1112 (1949).
4. P. R. O'Connor and G. T. Seaborg, Phys. Rev. 74, 1189 (1948). ✓
5. I. Perlman, R. H. Goeckermann, D. H. Templeton, and J. J. Howland, Phys. Rev. 72, 352 (1947).
6. R. E. Batzel and G. T. Seaborg, Phys. Rev. 79, 528 (1950).
7. Y. Yamaguchi, Prog. Theor. Phys. 5, 143 (1950).
8. E. M. Douthett, University of California Radiation Laboratory Report UCRL-1244 (May, 1951).
9. B. J. Finkle, E. J. Hoagland, S. Katcoff, and N. Sugarman, National Nuclear Energy Series, Plutonium Project Record, Vol. 9, Div. IV, "Radiochemical Studies: The Fission Products," Paper No. 46 (McGraw-Hill Book Co., Inc., New York, 1951).
10. F. Suzor, Ann. phys. (12) 4, 269 (1949).
11. R. L. Aamodt, V. Petersen, and R. Phillips, private communication.
12. 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, 1949).
13. L. R. Zumwalt, U. S. Atomic Energy Commission Declassified Document MDDC-1346 (February 8, 1949).
14. B. P. Burt, Nucleonics 5, no. 2, 28-43 (1949).
15. L. Yaffe and K. M. Justus, J. Chem. Soc. (London), p. S341 (1949), Part V.
16. L. Malatesta, unpublished data.

17. W. Nervik and P. C. Stevenson, unpublished work.
18. M. Studier and R. James, unpublished data.
19. E. Potter and H. Robinson, unpublished data.
20. G. Rudstam, P. C. Stevenson, and R. L. Folger, unpublished work.
21. G. T. Seaborg and I. Perlman, Revs. Modern Phys. 20, 585 (1948).
22. Chart of the Nuclides, General Electric Research Laboratory, 1950.
23. G. Wilkinson and H. G. Hicks, Phys. Rev. 75, 1687 (1949).
24. Ibid., 79, 815 (1950).
25. Ibid., 75, 1370 (1949).
26. L. E. Glendenin, C. D. Coryell, and R. R. Edwards, National Nuclear Energy Series, Plutonium Project Record, Vol. 9, Div. IV, "Radiochemical Studies: The Fission Products," Paper No. 52 (McGraw-Hill Book Co., Inc., New York, 1951).
27. C. D. Coryell and N. Sugarman, Editors, National Nuclear Energy Series, Plutonium Project Record, Vol. 9, Div. IV, "Radiochemical Studies: The Fission Products," (McGraw-Hill Book Co., Inc., New York, 1951).
28. W. W. Meinke, University of California Radiation Laboratory Report UCRL-432 (August 30, 1949).
29. W. W. Scott, "Standard Methods of Chemical Analysis," (D. Van Nostrand Co., Inc., New York, 1949), edition 5, Vol. I, pp. 1058-9.
30. H. Hicks, private communication.
31. A. S. Newton, thesis, University of Michigan, 1941.
32. W. McDonell, private communication.
33. K. Street, Jr. and G. T. Seaborg, J. Am. Chem. Soc. 70, 4268 (1948).
34. E. R. Tompkins, U. S. Atomic Energy Commission Declassified Document AECD-1998 (October 31, 1947).

LIST OF ILLUSTRATIONS

Figure

1. The distribution of total fission product yields as a function of mass number.
2. Decay schemes for isobaric chains of mass 140 and of mass 166.
3. Standard curve of error histogram for mass 140 isobaric chain.
4. Standard curve of error histogram for mass 166 isobaric chain.
5. Hypothetical contour representation of bombardment product fission probabilities and contour representation of fission product yields.
6. Illustration for the fitting of a normal curve of error to isobaric yield data.
7. $E(y)/E(y-a)$ as a function of y for various a .

Fig. 1

MU 1288

Fig. 2

Fig. 3

Fig. 4

Fig. 5

MU 1287

Fig. 6

Fig. 7