Radiochemical Studies on the Fission of Th^{232} with Pile Neutrons*

A. TURKEVICH AND J. B. NIDAY
Argonne National Laboratory and Institute for Nuclear Studies, University of Chicago, Chicago, Illinois
(Received June 11, 1951)

The relative yields of more than twenty products in thorium fission have been determined radiochemically. Pile neutrons with an estimated effective average energy of 2.6 Mev were used. The data have been used to construct a complete fission yield curve for Th^{232}. This is compared with the yield curves of other fissionable nuclei. Thorium fission is similar to the neutron fission of U^{235}, U^{233}, Pu^{239}, and U^{238} in being highly asymmetric. With the neutrons used in this work the peak yields occur 110 times as frequently as symmetrical products.

I. INTRODUCTION

THE nuclear fission processes that have been observed to date can be classified roughly into two categories: those which follow directly from the original excited compound nucleus, and those which involve the prior emission of one or more light particles (usually neutrons). In the former case the fragments, after division, may give off neutrons. For heavy nuclei (Z equal to or greater than 90), spontaneous fission and fission induced by photons or neutrons of energy less than roughly 8 Mev fall into the first category; fission produced by photons or particles of higher energy as well as by charged particles falls into the second category. This paper reports on the study of the nuclear fission of Th^{232} with moderate energy neutrons[1] as an example of fission of the first variety.

One of the characteristics of a fission reaction is the large number of products formed. Those found in detectable yields cover a mass range of up to 90 units. The relative yields of these products are characteristic of the fissioning nuclide and the excitation energy. The most sensitive and detailed method of investigating the yield-mass curve resulting from fission is the radiochemical technique. By this method the relative yields of β-radioactive nuclear species with moderate or long lives can be determined; the yields of such species usually represent all of the yield for the particular mass number from fission of the first category. In the mass region of interest, almost every second mass number is represented by a suitable nuclide for radiochemical analysis so that the method can be much more detailed than most other methods. Although the errors can be quite large (up to $\sim$30 percent) because of the uncertainties of β-counting, these errors are independent of the absolute yield over the entire range of about 10^6.

Previous radiochemical studies on the products of the low energy fission of heavy nuclei have established rather completely the fission yield curves[2–6] of U^{235}, Pu^{239}, and U^{233}. In all these cases it has been demonstrated that the most probable mode of fission is not into equal fragments, symmetrical fission being one of the least probable modes. The main difference in the yield-mass curves of these nuclides appears to be a shift in the light group to take care of the varying mass of the fissioning nuclide while the heavy group remains relatively fixed in position.

The much less sensitive and detailed ionization chamber technique has been used to study the fission of many nuclides.[7] In particular, the fission of Th^{232} by fast neutrons has been investigated by this method by Jentschke[8] and by Fowler and Rosen.[9] Although these studies could not establish the detailed course of the yield curve, they indicated that the fission of Th^{232} with neutrons of energy not too much above the threshold is similar to the slow-neutron examples in that symmetric and very asymmetric fission are quite improbable, and that the widths of the peaks of the yield-mass curves are comparable.

The first radiochemical work on the fission of Th^{232} dates, of course, to pre-1939 days. Thorium, as well as uranium, when irradiated with neutrons, had been found to produce the complex set of radioactivities that were eventually clarified as arising from nuclear fission.[10] Even in this early work it was recognized that the phenomenon in thorium required the use of more energetic neutrons than in uranium.

Subsequent to the elucidation of the phenomenon of

* A preliminary report on this work was made at the American Physical Society Meeting, June, 1950, Mexico City [J. Niday and A. Turkevich, Phys. Rev. **80**. 136(A) (1950)].

[1] A radiochemical study of the fission of Th^{232} with 37.5-Mev alpha-particles has been made by A. S. Newton, Phys. Rev. **75**, 17 (1949). The original compound nucleus in this case is U^{236}, excited by such a large amount, however, that its break-up probably represents fission of the second variety.

[2] The Plutonium Project, Revs. Modern Phys. **18**, 513 (1946).

[3] *Radiochemical Studies: The Fission Products* (McGraw-Hill Book Company, Inc., New York, 1951), National Nuclear Energy Series, Div. IV, Vol. 9, Appendix B.

[4] W. E. Grummit and G. Wilkinson, Nature **161**, 520 (1948).

[5] L. Yaffe and C. E. MacKintosh, Can. J. Research **B25**, 371 (1947).

[6] Steinberg, Seiler, Goldstein, and Dudley, talk before Am. Assoc. Advancement Sci., December, 1947; U. S. AEC declassified document, MDDC 1632 (January 6, 1948), unpublished.

[7] For example, D. C. Brunton and G. C. Hanna, Phys. Rev. **75**, 990 (1949). This note gives references to much of the other work of this type.

[8] W. Jentschke, Z. Physik **120**, 165 (1943).

[9] J. L. Fowler and L. Rosen, Phys. Rev. **72**, 926 (1947).

[10] See L. A. Turner, Revs. Modern Phys. **12**, 1 (1940), for a review of the radiochemical work on uranium and thorium leading to the discovery of nuclear fission. This article summarizes also the prewar work.

nuclear fission, many individual fission products were isolated from neutron-irradiated thorium.[10] In general, these appeared to be the same ones that were present in uranium fission. During the war, Sugarman and coworkers[11] on the Manhattan Project began a study of the fission products of thorium, but the work was interrupted after demonstrating that all of the radioactive nuclides formed in U^{235} fission that were looked for were also found in Th^{232} fission. In fact, several fission products were found first in such isolated studies of thorium fission and later identified in U^{235} fission.

The fundamental nuclear data pertaining to the neutron fission of Th^{232} are rather meager. Thermal neutrons apparently cause no observable fission. The cross section reaches detectable values[12] at a neutron energy of 1.10 ± 0.05 Mev. At 2.5 Mev it is reported[13] to be 10^{-25} cm^2 compared with 5×10^{-25} cm^2 for U^{238}.

In this paper we report the relative yields of twenty-three masses produced in the fission of thorium by neutrons in a uranium pile. The radiochemical technique has been used. The results are sufficient to characterize the yield-mass curve rather completely and make possible a comparison of Th^{232} fission with other known examples of fission.

II. GENERAL EXPERIMENTAL PROCEDURE

A. Irradiation Conditions

The source of neutrons for this work was the Argonne heavy-water pile (CP-3, before reconstruction). The irradiations were performed in the "thimble" of this pile, i.e., close to the geometrical center of the lattice. Although the position in the thimble varied from one irradiation to another, the gross number of fissions per gram of thorium per kilowatt-hour of operation of the pile was constant within the errors of comparing bombardments (±10 percent), indicating that neither the variation in position nor the variation in size of the samples, nor the frequent presence of neighboring samples was affecting the irradiation conditions appreciably.

The thorium was irradiated in the chemical form of $Th(NO_3)_4\cdot4H_2O$ ("Baker's Analyzed"). The samples varied in weight from 30 to 60 grams and were enclosed in corked quartz containers. These quartz containers were wrapped in cadmium foil to reduce the activation of thorium or impurities by the intense thermal-neutron flux of the pile, and the entire assemblage was then placed in standard aluminum containers (~1 in. diameter).

In the average position of irradiation, the samples were a few inches away from four uranium rods; the space between was occupied by heavy water, aluminum, and other small samples being irradiated simultaneously. In such a position, besides the intense flux of thermal neutrons, there are present large numbers of fast neutrons from the fissions occurring in the neighboring uranium rods. The distribution in energies of the neutrons which actually effected fission in the thorium is not readily estimated. If it is assumed that these are the primary fission neutrons with energy above the thorium fission threshold (1.1 Mev), we calculate that half of the fissions are caused by neutrons of energy greater than 2.7 Mev.

The time of irradiation was adjusted to be convenient for the particular nuclides being studied. It varied from 10 minutes to several days. In cases where the pile operation was not steady, it was assumed that during a given irradiation the fission rate varied directly with the power level. Most of the irradiations were performed with the power level varying by not more than 25 percent.

The fission yields to be reported were determined from seventeen different irradiations carried out over a period of several years. In about half of these, a sample of normal uranium was irradiated with thermal neutrons at the same time as the thorium samples. These experiments (called "comparison experiments") gave the relative yields of several fission products in Th^{232} and U^{235} rather independently of counting efficiencies or of uncertainties in decay constants or irradiation conditions.

B. General Radiochemical Procedure

After irradiation, the samples were dissolved in hot water containing nitric acid, and aliquots of this solution were taken for separation of the various fission products. The determinations were usually made in duplicate in each experiment, and only infrequently was the same aliquot portion used for more than one fission product.

The fission products were isolated by the standard radiochemical procedure of adding a known amount of inactive isotopic carrier, encouraging "exchange" between the carrier and the tracer quantities of the fission products, and then purifying the element in question from the matrix (uranium or thorium salts) and from other fission-product radioactivities. The carrier element was finally precipitated in a form suitable for weighing and counting, and the fraction recovered was determined from the weight.

In general, the chemical procedures followed were patterned on those developed in the Manhattan Project.[14] The main modifications were those necessitated by starting with a thorium salt rather than a uranium salt and by having this material in rather large amounts. Particular changes in the analytical procedures will be noted in the discussion of the different nuclides.

The radioactivity of the purified fission products was

[11] Ballou, Burgus, Dial, Glendenin, Finston, Ravely, Schloss, and Sugarman, see reference 3, paper 225.

[12] W. E. Shoupp and J. E. Hill, Westinghouse Research Laboratory, Scientific Paper 1390. Haxby, Shoupp, Stephens, and Wells, Phys. Rev. **57**, 1088 (1940).

[13] Ladenburg, Kanner, Barschall, and Van Voorhis, Phys. Rev. **56**, 168 (1939).

[14] See reference 3, Part VI.

measured usually with a glass-walled (~45 mg/cm²) Eck-and-Krebs-type Geiger tube. In a few cases the end-mica-window-type Geiger tube was used. The radiochemically pure precipitate, usually 5 to 25 mg, was filtered on a 1.5-cm² filter paper disk which was mounted on standard cardboard cards and covered with Cellophane. The behavior of the measuring tube was monitored by use of a beta-standard.

The purity of the radioactivity isolated was checked by following its decay and by comparing the absorption properties in aluminum of the radiations with the known characteristics of the nuclide in question. In some cases the presence of other isotopic radioactive nuclides had to be taken into account.

The low fission rate of thorium in the pile, corresponding to an "effective thermal fission cross section" of about 1 millibarn, and the low fission yields of some of the nuclides studied, made the thermal-neutron activation of impurities particularly serious. In general, an attempt was made to look for those fission products that would not be interfered with by products of (n,γ) processes on stable isotopes. Also, neutron irradiations of the thorium salt were performed in the thermal column of the pile, where fast neutrons are few, to prove that the uranium level was not high enough to affect the results. However, samarium and arsenic activities formed by neutron activation of impurities proved large compared with those formed in the fission process. It seemed impractical to remove the small amounts of samarium responsible, and analysis for this fission product was abandoned. In the case of arsenic, however, the product of the (n,γ) reaction, As^{76}, has sufficiently different radiation characteristics to be distinguished from the fission product As^{77}, and corrections could therefore be made in the fission-product analysis for arsenic.

In the case of several other impurities it was demonstrated by more conventional analytical techniques that they were not present in interfering amounts.

C. Treatment of Data

Two types of experiments were performed in getting relative fission yields. In one type, samples of normal uranium were irradiated with slow neutrons in the pile simultaneously with the thorium samples. If two fission products (B and X) are isolated from both the uranium and thorium samples and counted at the same time and under comparable conditions, then their fission yield ratio in thorium relative to their yield ratio in uranium is independent of the duration of the irradiation, the decay time, the half-lives of the nuclides, and the detection efficiencies for the radiations. The two yield ratios are related to each other and to the observed activity of the two fission products by the equation:

$$\frac{Y_X^{Th}}{Y_B^{Th}} = \frac{Y_X^{U}}{Y_B^{U}} \cdot \frac{A_X^{Th}}{A_X^{U}} \cdot \frac{A_B^{U}}{A_B^{Th}}.$$

In this equation the letters Y and A designate fission yields and measured activities (corrected to the total sample); subscript letters differentiate the fission products in question; superscript symbols denote the fissioning nuclide, e.g., A_B^{Th} = the activity of fission product B in the thorium sample measured at a standard time.

The values assumed for the fission yields in uranium fission (Y_B^U, Y_X^U) were taken from the literature data or from a smooth curve interpolation of experimental data,[3] and are indicated in the table of results (Table I).

In general one fission product, Sr^{89}, was isolated from each bombardment, and all thorium yields were expressed relative to an arbitrary value for the yield of mass 89. The relative fission yields for Th^{232} from these comparison experiments are, of course, no more accurate than the values for U^{235} on which they are based.

About half of the fission products studied were not isolated from simultaneously irradiated uranium. In these cases the measured radioactivity had to be corrected for growth during and decay subsequent to the irradiation, and for the genetic characteristics of the beta-decay chain. Besides this, the radioactivity also had to be corrected for differences in detection efficiencies for the radiations because of absorption in the sample covering, air, and counter walls, and scattering and self-absorption in the sample itself.

The first corrections are straightforward. The half-lives and genetic relationships used in the calculations were usually those of the *Table of Fission Products* issued by the Plutonium Project.[2,15] The corrections for absorption in the counter tube walls were made on the assumption that the beta-rays were being absorbed exponentially. The absorption coefficients used were obtained from aluminum absorption curves taken on end-window Geiger tubes, but were corrected empirically to apply to the cylindrical geometry of the "Eck and Krebs" tubes. The wall thicknesses of the tubes were estimated from the counting rate of a uranium standard. The relation of this counting rate to wall thickness was established from tubes where the wall thickness was available. The estimated wall thicknesses ranged from 40 to 52 mg/cm², and it was felt that they were known to ±5 mg/cm². The weight of Cellophane covering (~2.6 mg/cm²) and air (~1 mg/cm²) was also included in the absorption correction.

In estimating the effects of self-absorption and self-scattering and back-scattering from the samples,[16] no correction at all was applied if the sample weight, expressed as mg/cm², was less than half the half-thickness of the radiations involved. If the sample weight was greater than this, a self-absorption correction was

[15] The Plutonium Project, J. Am. Chem. Soc. 68, 2411 (1946); see also reference 3, Appendices A and C.

[16] Engelkemeir, Seiler, Steinberg, and Winsberg, see reference 3, Paper 4.

applied according to the formula,[17]

$$K = (1 - e^{-\mu d})/\mu d.$$

K is the fraction of the radiations with absorption coefficient μ emerging from a sample of weight d mg/cm^2.

D. Evaluation of Errors

The easily evaluated errors of timing, level of irradiation, uncertainties in half-lives of the fission products, etc., are unfortunately small compared with others that are not easily estimated. It is well known that the radiochemical method may not yield quantitative results if the element in question can exist in different forms in solution. For example, the different valence states of iodine in solution do not exchange readily.[18] In this work an effort was made to minimize trouble from this source. Even so, the iodine and rhodium results scatter much more than the others. In the case of molybdenum, where exchange troubles were at first encountered, conditions of analysis were found which gave consistent results.

Errors have been assigned to the reported fission yields which take into account the number of experiments performed, the agreement between duplicate determinations, the sensitivity of the relative yields to errors in beta-absorption corrections, and suspected chemical exchange troubles. These errors thus give the range within which we believe the true values lie.

III. COMMENTS ON INDIVIDUAL DETERMINATIONS

In general, the chemical procedures and analysis of the data were straightforward. There are given here the barest details except where warranted by specific circumstances.

Zinc (49-hr $Zn^{72} \rightarrow$ 14.3-hr Ga^{72})

The procedure used was almost identical with that of Siegel and Glendenin,[19] which makes use of the precipitation of $ZnHg(SCN)_4$, and scavenging operations. The original separation of zinc from the thorium, however, was made by precipitation of ZnS from an ammonium carbonate solution of the thorium nitrate.

Because of the low fission yield of this nuclide, quite low counting rates were obtained. The characteristic growth and decay of the chain, could not, however, be mistaken.

Gallium (5-hr Ga^{73})

The procedure used was practically identical with that of Siegel and Glendenin,[20] which depends primarily on the ether extraction of gallium from $6M$ HCl. Besides scavenging operations, two precipitations of gallium ferrocyanide were made. Unfortunately, the product was contaminated, apparently with 67-hr Mo^{99}.

Germanium and Arsenic (Mass 77 Chain)

The known characteristics[15] of the β-decay chain with mass 77 are:

$$\begin{array}{l} \text{59-sec } Ge^{77} \searrow \\ \qquad\qquad\quad \text{40-hr } As^{77} \rightarrow \text{stable } Se^{77}. \\ \text{12-hr } Ge^{77} \nearrow \end{array}$$

The yield of 12-hr Ge^{77} in Th^{232} fission was measured in two experiments. The germanium was isolated from the solution of irradiated thorium nitrate by first precipitating GeS_2 from $6N$ H_2SO_4 and then following the radiochemical procedure of Winsberg.[21] This depends primarily on two distillations of $GeCl_4$ from an HCl solution in a stream of chlorine. The latter keeps arsenic as the relatively nonvolatile $AsCl_5$. The arsenic is distilled later as $AsCl_3$.

As is well known[22,23] a part of the chain of mass 77 decays through the 59-sec isomer of Ge^{77}. The fraction of the total As^{77} that is formed by decay of the 59-sec isomer of Ge^{77} is reported as 0.59 for U^{235} and 0.55 for U^{233} fission. This fraction is determined by the yield of 12-hr Ge^{77} and the additional measurement of total 40-hr As^{77} formed in fission. In our work,[24] the 38-hr As^{77} isolated from the irradiated thorium nitrate showed radiochemical contamination from 26.8-hr As^{76} formed by (n,γ) processes on minute arsenic impurities in the thorium nitrate. About half of the measured arsenic radioactivity was this unwanted As^{76}. Although the amount present could be estimated from the absorption characteristics of the radiations (38-hr As^{77} has a 0.7-Mev β^-; the 26.8-hr. As^{76} has much more energetic beta-rays—up to 3 Mev), the resulting yield of As^{77} is appreciably more uncertain than that of Ge^{77}. Two experiments in this work gave values of 0.53 and 0.65 for the fraction of the As^{77} that does not come from 12-hr Ge^{77}. Thus, it appears as if the branching in the chain of mass 77 is the same in Th^{232} fission as it is in the slow neutron fission of U^{235} and U^{233}. The total yield of mass 77 is calculated from the yield of 12-hr Ge^{77} and a branching ratio of 0.57.

Bromine (2.4-hr Br^{83})

The procedure used was the same as that of Glendenin, Edwards, and Gest[25] which involved the addition of BrO_3^- carrier, reduction with H_2S, and then repeated oxidation-reduction cycles with extractions of the Br_2 into CCl_4. Several of these cycles were made under con-

[17] Henriques, Kistiakowsky, Margnetti, and Schneider, Ind. Eng. Chem., Anal. Ed. 18, 349 (1946).
[18] See, for example, W. H. Burgus and T. H. Davies, reference 3, Paper 19.
[19] J. M. Siegel and L. E. Glendenin, see reference 3, Paper 226.
[20] J. M. Siegel and L. E. Glendenin, see reference 3, Paper 227.
[21] L. Winsberg, see reference 3, Paper 228.
[22] E. P. Steinberg and D. W. Engelkemeir, see reference 3, Paper 54.
[23] J. Arnold and N. Sugarman, J. Chem. Phys. 15, 703 (1947).
[24] Although As^{77} is assigned a half-life of 40 hours in all standard compilations, the present study indicates that the proper half-life is closer to 38 hours, in accord with the work of N. Sugarman (reference 23, and private communication).
[25] Glendenin, Edwards, and Gest, see reference 3, Paper 232.

ditions that decontaminated the bromine from fission iodine. The calculations were made assuming[28] that 27/48 of the bromine came from 67-sec Se^{83} and the rest from 25-min Se^{83} as in U^{235} fission.

Strontium (53-day Sr^{89} and 9.7-hr Sr^{91}) (Comparison Experiments)

The procedure used for isolating strontium was essentially that of Glendenin,[26] although minor modifications were made from time to time. This procedure utilizes the fairly specific separation of strontium and barium nitrates from cold fuming nitric acid, the removal of barium as the chromate from a buffered acetate solution (pH$\sim$5), and hydroxide scavengings. In the first four experiments the final precipitate was strontium oxalate; in later experiments and in all the comparison experiments, $SrCO_3$ was used.[27]

Strontium (25-yr Sr^{90}→65-hr Y^{90})

This chain was determined by isolating strontium radiochemically (see above) and then milking the 65-hr Y^{90} daughter after it had grown in. Since rather large amounts of thorium had to be used to get enough of this activity, the thorium was first precipitated as the hydroxide, and the radiostrontium and its carrier were isolated from the supernate and washings.

The removal of the yttrium from the $SrCO_3$ precipitates consisted simply of solution in acid, several precipitations of the hydroxide (with strontium hold-back carrier), and final yttrium oxalate precipitation.

The half-life of the long-lived member of this chain, Sr^{90}, is reported as 25 years in standard compilations, but is apparently based partly on expected yields in U^{235} and Pu^{239} fission.[28] The recent observation[29] of actual decay of Sr^{90} indicates a half-life of 19.9±0.3 years. If this is the correct half-life, the value reported here for the fission yield of this chain in Th^{232} fission should be lowered by 20 percent, and definite irregularities in the yield-mass curves of U^{235}, Pu^{239}, and Th^{232} are indicated.

Zirconium (17-hr Zr^{97}) (Comparison Experiments)

The procedure for separating zirconium was essentially that of Hume,[30] which consists of complexing the zirconium with F^-, scavenging with LaF_3, precipitating $BaZrF_6$ several times, and dissolving in H_3BO_3. The zirconium is finally mounted and counted as the oxide.

In spite of the cadmium shielding around the thorium samples, very large amounts of Pa^{233} were formed from the Th^{232} by neutron capture. Since the attempts to separate protactinium and zirconium were not too successful at the time, the counting was done through 136 mg/cm^2 aluminum, which greatly emphasizes the Zr^{97} radiations.

[26] L. E. Glendenin, see reference 3, Paper 236.
[27] E. Hoagland, see reference 3, Page 237.
[28] See reference 3, R. W. Nottorf, Paper 77; and L. E. Glendenin and C. D. Coryell, Paper 78.
[29] R. I. Powers and A. F. Voigt, Phys. Rev. **79**, 175 (1950).
[30] D. N. Hume, see reference 3, Paper 245.

Molybdenum (67-hr Mo^{99}) (Comparison Experiments)

The chemical procedure was modified from that of Ballou[31] which consisted of specific precipitations of molybdenum with α-benzoinoxime and hydroxide scavengings after decomposition of the α-benzoinoxime precipitate in HNO_3-HClO_4. It was found necessary to dissolve the irradiated $Th(NO_3)_4\cdot 4H_2O$ in 6N HNO_3 to avoid loss of tracer molybdenum and also desirable to have a large excess of NH_4OH present during the hydroxide scavengings.

A final precipitation of $PbMoO_4$ from a buffered solution was used,[32] rather than Ag_2MoO_4.

Ruthenium[33] (42-day Ru^{103} and 1-yr Ru^{106}→30-sec Rh^{106}) (Comparison Experiments)

After ruthenium carrier was added to the matrix solutions, ruthenium metal was precipitated with zinc and magnesium. The metal was dissolved after KOH fusion, and the regular procedure of Glendenin based on RuO_4 distillations from perchloric acid was used.[34]

Since both Ru^{103} and Ru^{106} and its daughter Rh^{106} are present in the isolated ruthenium, the relative contributions of the two chains to the radioactivity had to be estimated either from the absorption characteristics or from the decay curve. Both methods were used. Since in both methods Ru^{103} is obtained by subtracting the contribution of chain 106, its yield carries a slightly higher estimate of error.

Rhodium (36.5-hr Rh^{105}) (Comparison Experiments)

In the case of rhodium, the use of procedures based on that of Ballou,[35] depending primarily on pyridine extractions of the rhodium, did not give satisfactory results. The presence of 36.5-hr Rh^{105} in thorium fission was definitely established although the yields varied among experiments and sometimes in duplicate samples within an experiment. These fluctuations are attributed to incomplete exchange between the added rhodium carrier and radiorhodium.

Palladium (13.4-hr Pd^{109} and 21-hr Pd^{112}→3.2-hr Ag^{112}) (Comparison Experiments[36])

The chemical procedure was essentially that of Seiler.[37] The first step in isolating the palladium from the thorium solution was to add carrier and then pour the entire solution into strong NH_4OH. This precipitated the thorium while keeping the palladium in solution. The main part of the procedure involved four dimethylglyoxime precipitations, interspersed with scavengings with $ZrO(OH)_2$ and AgCl.

[31] N. E. Ballou, see reference 3, Paper 257.
[32] Editor's note, Paper 209 of reference 3.
[33] We are indebted to Mr. Salter for the help in the chemical analyses and calculations on this fission product.
[34] L. E. Glendenin, Paper 260 of reference 3.
[35] N. E. Ballou, Paper 263 of reference 3.
[36] We are indebted to Mr. M. Kalkstein for help in these analyses.
[37] J. A. Seiler, Paper 264 of reference 3.

The yield of chain 112 was calculated from counting data taken through 355 mg/cm² of aluminum to absorb the radiation of Pd^{109}. The yield of chain 109 was obtained by least-squares analysis of the complex curve obtained with no added absorber, assuming the half-lives to be 13.4 hours for Pd^{109}, 21 hours for Pd^{112}, and 3.2 hours for Ag^{112}.

The literature values[3,15] of the yields in U^{235} fission are somewhat conflicting. The values chosen and listed in Table I were the result of consultation with E. P. Steinberg.[38]

Silver (7.5-day Ag^{111})

The procedure used was modified from that of Glendenin[39] in which silver is precipitated as the chloride, scavenged in ammoniacal solutions and collected as Ag_2S. Use was made of the solubility of AgCl in strong HCl and of precipitation by dilution in the presence of palladium and cadmium holdback carriers. Small amounts of bromide and iodide carriers were also used during the ammoniacal scavengings.

Cadmium (2.33-day Cd^{115}→4.53-hr In^{115m} and 43-day Cd^{115m})

The procedure used was essentially that of Metcalf,[40] which is based on precipitations of CdS from dilute HCl solution and scavenging with basic ferric acetate and with PdS. The first step consisted of precipitation of CdS from a solution of thorium complexed with $(NH_4)_2CO_3$.

Iodine (8.0-day I^{131} and 2.4-hr I^{132})

The chemical procedure used was similar to that of Glendenin and Metcalf.[41] The thorium was complexed with $(NH_4)_2CO_3$, the iodide carrier oxidized to periodate with NaClO, and after acidification reduced to I_2 with $NH_2OH \cdot HCl$. The iodine was extracted into CCl_4 (BrO_3^- goes to Br^- and does not extract). The iodine was then extracted into water with $NaHSO_3$, oxidized with $NaNO_2$ (which does not oxidize Br^-), and re-extracted with CCl_4. The final precipitate was AgCl.

Caesium (33-yr Cs^{137} and 13.7-day Cs^{136}) (Comparison Experiment)

One experiment was performed to get the yield of 33-yr Cs^{137} in thorium fission and to get information on the yield of the shielded nuclide Cs^{136} (13.7-day). The radiochemical purification, following the suggestions of Glendenin and Nelson,[42] was based on repeated silicotungstate and perchlorate precipitations of the cesium interspersed with scavenging operations. In this experiment the samples were demonstrated to be radiochemically pure by chemical recycling.

The yield of the 33-yr Cs^{137} was determined from the activity after the 13.7-day Cs^{136} had decayed away. There was markedly less of this 13.7-day component in the samples isolated from thorium than in those isolated from uranium. Unfortunately, there was not enough activity to emphasize this component by counting through absorber, so the gross decay curves were analyzed by least squares into 13.7-day and 33-yr components.

The average of three samples gave, for the yield of the shielded isotope (Cs^{136}) relative to the yield of 33-yr Cs^{137} in thorium fission, only one quarter of the corresponding quantity in uranium fission. The sensitivity of the experiment to possible short-lived impurities makes us place somewhat larger negative than positive limits of error on this quantity.

Barium (12.8-day Ba^{140}→40.0-hr La^{140})

The barium separations were essentially a combination of two methods by Glendenin utilizing the separation of $BaCl_2$ by HCl-ether solution[43] and of barium and strontium nitrates by fuming HNO_3, $Fe(OH)_3$ scavengings and $BaCrO_4$ precipitation.[26] In the first experiment the nitrate separation was not used; in all the others both purifications were used and the $BaCrO_4$ fractional precipitation technique initiated by Hahn and Strassman[44] was used in the final separation to reduce the contamination of barium by the radium isotopes from the natural decay of the thorium. The yield of the chain 140 was calculated from the counting rate of the barium extrapolated to the time of last $La(OH)_3$ precipitation.

Cerium (28-day Ce^{141} and 275-day Ce^{144})

The procedure used was essentially that of Boldridge and Hume,[45] which is based on separation of cerium and lanthanum fluorides in the presence of zirconium holdback carrier, several precipitations of $Ce(IO_3)_4$ after oxidation with BrO_3^-, solution of the precipitate by reduction to cerous ion with H_2O_2, scavengings with $Zr(IO_3)_4$, and finally precipitation as cerium oxalate. In two experiments, the first step consisted of the separation of cerium carbonate from the thorium complex in saturated $(NH_4)_2CO_3$ solution; in the third experiment, $Th(IO_3)_4$ was precipitated away from cerium reduced to the cerous state by H_2O_2.

IV. RESULTS

As discussed above, this work determined only relative fission yields. Sr^{89} was isolated in each experiment, and the yield of each nuclide investigated was calculated, assuming a fission yield of 6.7 percent[46] for Sr^{89}.

[38] E. P. Steinberg, Argonne National Laboratory, private communication.
[39] L. E. Glendenin, Paper 267 of reference 3.
[40] R. P. Metcalf, Paper 268 of reference 3.
[41] L. E. Glendenin and R. P. Metcalf, Paper 278 of reference 3.
[42] L. E. Glendenin and C. M. Nelson, Paper 283 of reference 3.
[43] L. E. Glendenin, Paper 288 of reference 3.
[44] O. Hahn and F. Strassman, Naturwiss. **27**, 89 (1939); also N. Sugarman and co-workers, reference 11.
[45] W. F. Boldridge and D. N. Hume, Paper 294 of reference 3.
[46] The value of 6.7 percent for the yield of Sr^{89} was chosen in order to give an integral under the total smooth yield-mass curve of 200 percent.

TABLE I. Fission yields from Th^{232} and pile neutrons.

1 Mass number	2 Nuclides isolated and measured	3 Yields from U^{235} (slow) neutron fission)[a] percent	4 Yields from Th^{232} (pile neutron fission)[b] percent	5 Estimated reliability percent
72	49-hr Zn→14.3-hr Ga	0.000015	0.00033	±0.00008
73	5-hr Ga	0.00010	0.00045	±0.00022
77	12-hr Ge→38-hr As	0.0037	0.009	±0.002
	Total 38-hr As	0.0091	0.020	±0.007
83	2.4-hr Br	0.48	1.9	±0.45
89	53-day Sr	4.6	6.7	±0.7
90	25-yr Sr→65-hr Y		6.1	±1.2
91	9.7-hr Sr	5.0	6.4*	±0.7
97	17-hr Zr	6.1	5.4*	±0.8
99	67-hr Mo	6.2	2.9*	±0.3
103	42-day Ru	3.7	0.20*	±0.07
105	36.5-hr Rh	0.9	0.07*	±0.02
106	1-yr Ru→30-sec Rh	0.5	0.058*	±0.006
109	13.4-hr Pd	0.028	0.053*	±0.010
111	7.5-day Ag	0.018	0.052	±0.010
112	21-hr Pd→3.2-hr Ag	0.011	0.065*	±0.010
115	2.33-day Cd→4.53-hr In^m	0.011	0.072	±0.014
	43-day Cd^m	0.0008	0.003	±0.0015
	Total chain	0.012	0.075	±0.015
131	8.0-day I	2.8	1.2	±0.6
132	77-hr Te→2.4-hr I	4.4	2.4	±0.7
136	13.7-day Cs	0.0062	0.0017*	$^{+0.0009}_{-0.0017}$
137	33-yr Cs	(6.2)[c]	6.6*	±1.0
140	12.8-day Ba→40-hr La	6.17	6.2	±2.0
141	28-day Ce	5.7	9.0	±3.0
144	275-day Ce→17-min Pr	5.3	7.1	±1.0

[a] The yields for U^{235} with slow neutrons are taken from the compilation in Vol. 9 of reference 3.
[b] The yields with an asterisk were obtained in comparison-type experiments. The yields listed depend directly on the assumption that the corresponding yields in the slow-neutron fission of U^{235} are correct.
[c] Fission yield of Cs^{137} estimated from smooth fission yield curve (reference 3) for U^{235}.

The fission yields thus calculated are presented in Table I. Opposite each mass number are listed the radioactive species isolated or measured. Column 3 lists the yields[3] in U^{235} fission with slow neutrons. Column 4 presents our observed yields from the fission of Th^{232} with pile neutrons. Values accompanied by an asterisk were obtained in comparison experiments. These yields depend directly on the corresponding yields in U^{235}. The last column gives our estimate of the limits of error in the thorium fission yields. In the case of the comparison experiments these errors do not contain the uncertainty arising from possible errors in the U^{235} yield of this chain.

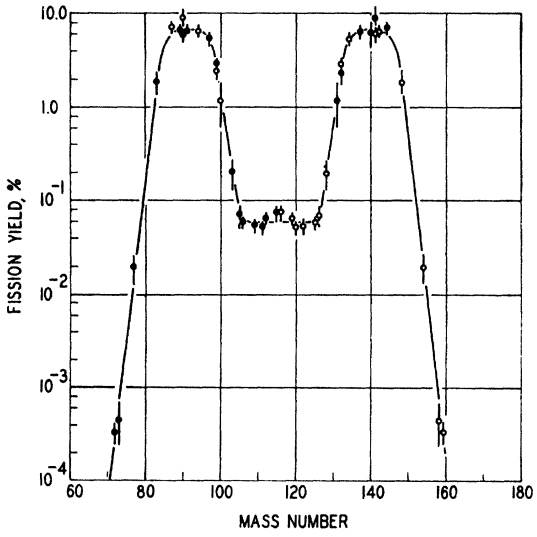

FIG. 1. Yield-mass curve for fission of Th^{232} with pile neutrons, normalized to 200 percent yield (assuming 2 neutrons given off). Solid circles represent experimental data, open circles represent the mirror points (231-A).

Since more than half of the fission yields have been determined for nuclides with mass numbers lighter than 116, a complete fission yield curve is best constructed by assuming that all fissions involve the formation of only two heavy particles,[47] and that a constant number of neutrons (we have arbitrarily assumed 2.0) are emitted. On these assumptions the yields of masses A and 231-A are equal. The data treated in this way are presented in Fig. 1, with a solid point indicating an experimental determination and an open circle representing the same yield for the mirror mass. Matching of the data is sensitive to the choice of the number of neutrons emitted only in the mass regions 97–105 and 126–134. Although the estimated errors here are rather large, it appears that fission into fragments with masses in these regions cannot be associated on the average with the emission of more than 2.5 or less than 1.5 neutrons.

Within estimated errors, the points lie on a smooth curve of the familiar "double-humped" shape. The maxima are at masses 91 and 140, giving 140/91 = 1.54 for the most probable mass ratio. The widths of the peaks at half-height are 14 mass units. Products of symmetrical or nearly symmetrical fission occur 110 times less frequently than the most probable products.

The yield curve in the mass region near symmetrical fission is very flat compared with the corresponding curves for U^{233}, U^{235}, or Pu^{239}. Unfortunately, the experimental error in the yield of Cd^{115} is large, and so it is impossible to say whether there is a real subsidiary maximum in the region of symmetrical fission. The rather sharp transition from the steep side of the peak to the rather flat trough appears real, however.

The experimental data, of course, give only relative yields. The absolute values in Table I were obtained by requiring that the smooth curve through the points account for all of the fissions, i.e., that the integral under the yield-mass curve give 200 percent. The most probable yield (from the smooth curve) comes out to be 6.8 percent.

V. DISCUSSION

The mass ratio, 1.54, for the most probable mode of fission of Th^{232} with pile neutrons, agrees with the

[47] There have been numerous attempts to detect nuclear fission into three or more heavy fragments by radiochemical and ionization chamber studies and by examination of fission tracks in photographic plates. It appears as if the frequency of such events in less than a few percent of all fissions. See K. W. Allen and J. T. Dewan, Phys. Rev. **82**, 527 (1951); L. Marshall, Phys. Rev. **75**, 1339 (1939).

ionization chamber studies of thorium fission,[8,9] which gave 1.51 and 1.59 for the ratio of most probable energies. It has been shown[7] that the widths of the peaks in the yield-mass curves are not directly comparable to the widths of the energy peaks in ionization chamber studies because of the distribution in the energy of fission even for a fixed mass ratio.

The characteristics of the yield curve for Th^{232} are compared with those of the yield curves[48] for other neutron fissionable nuclides in Table II. The comparison between the lightest and heaviest members of this set (Th^{232} and Pu^{239}) is presented also in Fig. 2, which shows the smooth yield curves for these two nuclides. The effect of varying the mass of the fissioning nucleus upon the yield-mass curve is illustrated in Table II and Fig. 2. Most of the change is a shift of the light group, the heavy group remaining fixed in position within a few mass units. The widths at half-height of the peaks of the yield-mass curves are all close to 15 mass units. There may be a trend to slightly wider peaks for the heavier nuclei.

The observed ratios of most probable yields to

TABLE II. Characteristics of yield-mass curves of different heavy nuclides fissionable with neutrons.[a]

1 Nuclide	2 Most probable light mass	3 Most probable heavy mass	4 Ratio of most probable masses	5 Mass width at half-height	6 Ratio of peak to trough yields
Th^{232}	91	140	1.54	14	110[b]
U^{233}	93	137	1.48	14	400
U^{235}	97	138	1.42	15	600
U^{238}	98	140	1.43	17	100[b]
Pu^{239}	99	138	1.39	16	140

[a] See reference 48. [b] Fast neutron fission.

yields for symmetrical division are also listed in Table II. Except for Pu^{239} (where the depth of the trough is determined by only one experimental point,[3] not necessarily at the minimum), the trough appears to be appreciably higher for U^{238} and Th^{232} fission than for nuclides fissionable with thermal neutrons. This may be accounted for by the following argument:

In the fission of U^{235} with slow neutrons, the decomposition of the excited compound nucleus U^{236} is relatively slow, as evidenced by appreciable competition from gamma-emission leading to the formation of U^{236} in its ground state.[49] At the effective threshold for Th^{232} fission with neutrons ($\sim$1.1 Mev) the fission break-up of the excited Th^{233} nucleus must compete primarily with neutron emission and is therefore much faster than the break-up of the excited nucleus in the slow neutron fission of U^{235}. In addition, the average energy of the neutrons causing fission in our experiments on Th^{232} has been estimated as about 2.6 Mev; thus it is appreciably

[48] The data for U^{235} and Pu^{239} are from reference 3; for U^{238}, see subsequently in text; the data for U^{233} are from reference 6.

[49] Can. J. Research **29**, 203 (1951); Ghiorso, Brittain, Manning, and Seaborg, Phys. Rev. **82**, 558 (1951).

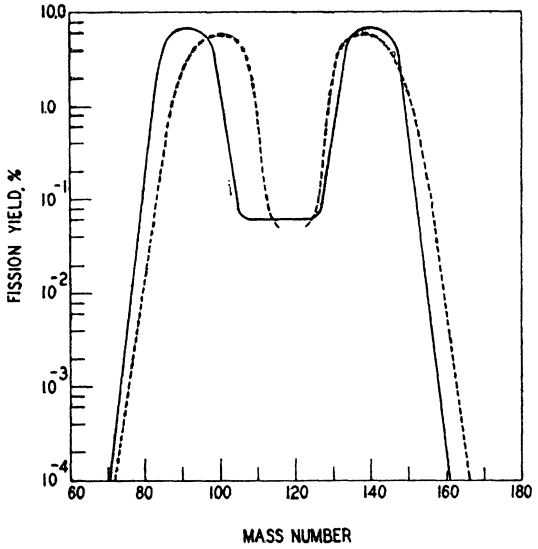

FIG. 2. Smooth yield-mass curve for fission of Th^{232} (solid line) compared with the curve for Pu^{239} (dashed line). The plutonium curve is from reference 3.

higher than the "threshold" energy. The U^{238} fission yields[50] were obtained under similar conditions. An increase in the neutron energy causing fission is known to raise the yield of symmetrical products.[51] Therefore,

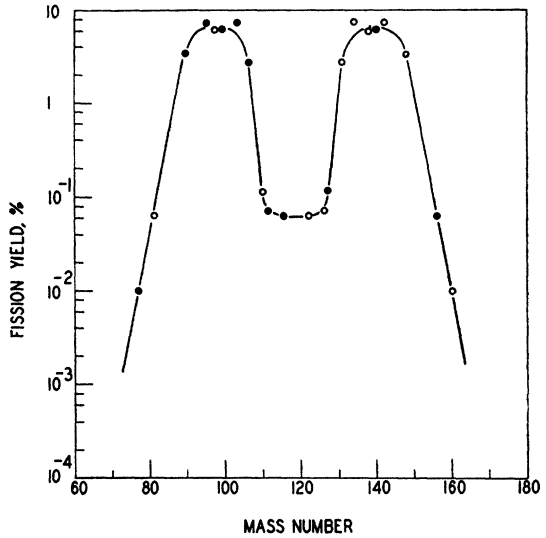

FIG. 3. Yield-mass curve for fission of U^{238} with pile neutrons constructed assuming binary fissions with two neutrons emitted (not normalized). Solid circles represent experimental data; open circles represent the mirror points (237-A). The experimental data are from reference 50.

[50] Engelkemeir, Seiler, Steinberg, and Winsberg, Paper 218, of reference 3.

[51] This effect of neutron energy on the ratio of peak to trough yields has been established for U^{235} (R. W. Spence, Brookhaven Conference Report BNL-C-9, June 14, 15, 1949), for Pu^{239} (Engelkemeir, Freedman, Seiler, Steinberg, and Winsberg, Paper 204, see reference 3), and for Th^{232} (A. Turkevich, talk before Am. Assoc. Advancement Sci. meeting, Chicago, December 1, 1947, U. S. AEC declassified document, MDDC 1568).

the higher troughs observed in the case of U^{238} and Th^{232} fission are reasonable in view of the energy of the neutrons being used. Specifically, they are not inconsistent with a constant ratio of peak to trough in the fission of all heavy nuclei at excitations at which the rate of break-up of the compound nucleus into fission fragments is comparable.

The radiochemical U^{238} fission yield data of Engelkemeir, Seiler, Steinberg, and Winsberg[50] is presented in Fig. 3 in a manner comparable to that used for our data in Fig. 1 (assuming binary fission with loss of two neutrons). The rather flat regions near symmetrical fissions in Figs. 1 and 3 suggest that perhaps the observed curves are superpositions of two yield curves, one the familiar "double-humped "curve, whose shape and absolute values are not very sensitive to neutron energy, the other a yield curve with a rather broad maximum at symmetrical fission. The peak in the latter curve would be much lower than those in the asymmetric type, but the absolute values here would increase with increasing neutron energy.

The results reported in Table I also give a little information on the charge distribution in Th^{232} fission as compared with U^{235} or Pu^{239} fission. Because the neutron-to-proton ratio in Th^{232} is higher than that in U^{235} and Pu^{239}, slightly longer fission chains are expected in Th^{232} fission. For this reason there should be no change in the relative yields of isomers close to the end of a beta-chain, since these would be formed primarily by beta-decay of a fission product with lower charge rather than directly in the fission process. Within experimental error, this is borne out in the cases of isomers in the chains of mass 77 and 115.

On the other hand, because of the higher neutron to proton ratio in Th^{232} relative to U^{235} and Pu^{239}, a lower yield of shielded isotopes is to be expected.[52] In the one case investigated (Cs^{136}) this expectation was also realized: in Th^{232} fission, the yield of Cs^{136} is apparently no greater than one quarter of that in U^{235} fission with slow neutrons. The theory of Glendenin[52] predicts for Cs^{136} a yield in Th^{232} fission about 20 times lower than in U^{235} fission.

[52] L. E. Glendenin, Ph.D. thesis, Massachusetts Institute of Technology (July 29, 1949), unpublished.

PHYSICAL REVIEW VOLUME 84, NUMBER 1 OCTOBER 1, 1951

Neutron-Capture Theory of Element Formation in an Expanding Universe*†‡

RALPH A. ALPHER AND ROBERT C. HERMAN
Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland.

(Received June 11, 1951)

The neutron-capture theory of element formation by non-equilibrium processes has been extended to include explicitly the effect of the expansion of the universe, and the resulting equations have been solved on an electronic digital computing machine. Inclusion of the universal expansion is found to require an increase by a factor of five of the density of matter chosen for the start of the element-forming process over that previously found necessary to represent the observed relative abundance distribution of elements in a static universe. The following physical conditions lead to agreement in the over-all trend of theoretical with observed abundances: the element-forming process is taken to start at ~140 sec after the "beginning" of the universal expansion; at this time the temperature is $\sim 1.3\times 10^{9}$°K$\cong$0.11 Mev, the neutron-proton ratio is 7.33:1, and the density of matter is $\sim 0.9\times 10^{-6}$ g/cm^3. This density value includes a correction made to account for the effect of groupiing together nuclear species in order to reduce the number of defferential equations required to describe the neutron-capture procss.

The effect of the choice of an initial neutron-proton ratio on the other physical conditions involved in representing the observed relative abundance data is considered. A neutron-proton starting ratio of 1:4, recently found by Hayashi to result from the interactions between matter and radiation in the pre-element-forming phase of the expanding universe, is shown to lead to some difficulties.

In an Appendix, Dr. T. H. Berlin, of The Johns Hopkins University, shows that the differential equations describing the element-forming process can be solved in closed form for the static case by the use of laplace transforms. However, the inclus on of the universal expansion precludes solution in closed form.

I. INTRODUCTION

THE work described in this paper serves to complete one aspect of the description of the origin and observed relative abundance distribution of the chemical elements according to a non-equilibrium neutron-capture theory. Calculations have been made of the dependence on atomic weight of the relative abundance distribution of nuclear species which results if the effect of the expansion of the universe is explicitly taken into account in the formation process. In previously reported work[1,2] the process of element formation by successive neutron captures was examined for a static universe; and it was shown that the general

* This work was supported by the U. S. Navy Bureau of Ordnance.

† Preliminary accounts of this work were presented at the New York meeting of the American Physical Society, February, 1951, Phys. Rev. 82, 296(A) (1951), and at the Washington meeting, April, 1951, Phys. Rev. 83, 236(T) (1951).

‡ This paper includes an Appendix by Dr. T. H. Berlin, Department of Physics, The Johns Hopkins University, on the exact solution of equations describing element formation in a static universe according to the neutron-capture theory.

[1] R. A. Alpher and R. C. Herman, Phys. Rev. 74, 1737 (1948).
[2] R. A. Alpher and R. C. Herman, Revs. Modern Phys. 22, 153 (1950).