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THE FISSION OF LUTETIUM AT LOW EXCITATION ENERGY

Herman W. André

MASTER

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THE FISSION OF LUTETIUM AT LOW EXCITATION ENERGY

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Submitted to the Faculty

of

Purdue University

by

Herman W. Andre

In Partial Fulfillment of the

Requirements for the Degree

of

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ABSTRACT

Andre, Herman W. Ph.D., Purdue University, June 1964. The Fission of Lutetium at Low Excitation Energy. Major Professor: James W. Cobble.

The fission of lutetium was studied by bombarding thick targets of highly purified Lu_2O_3 with 39.6 Mev helium ions. The fission products were chemically separated and purified and their activities counted in low-level beta counters. The absolute fission cross sections were calculated by assuming an excitation function based upon the fission of gold at this energy. To ensure that the fission products measured did not result from the fission of heavy element impurities, a series of activation experiments were conducted.

The principal observations resulting from this study are:

- 1) This research has experimentally demonstrated the presence of fission in lutetium at low excitation energy.
- 2) The mass yield curve at an excitation energy of 36.3 Mev is symmetric about mass 89 with a full-width-at-half-maximum of about 17.5 mass units. It appears that an average of one neutron is emitted per fission event.
- 3) The total fission cross section at 36.3 Mev is estimated to be 1.5 ± 0.5 microbarns.

4) The enhanced fissionability of lutetium compared to other (higher Z) elements is attributed to the significant ground state distortion of the fissioning nucleus as indicated by its large quadrupole moment.

Detailed explanations of the experimental procedures and of the chemical separations and purifications are given.

THE POSSIBLE ENHANCEMENT OF FISSION BY NUCLEAR DISTORTION*

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The purpose of this communication is to report the results of an investigation of the fission of Lu^{175} induced by 39.6 Mev helium ions. It appears that this study has demonstrated that nuclei having permanent nuclear distortions will be more likely to undergo the fission process. Hill and Wheeler¹ predicted in 1953 that the same factors which cause a large permanent quadrupole moment could be expected to lower the fission barrier height by a few Mev. Although the same effect should be present in the fission of distorted heavy elements ($Z \geq 90$), it would be too subtle to be evident there since greater than 80% of the total cross section already leads to fission, even at modest excitation energies.

In recent years, developments in both radiochemical and solid state techniques have made it possible to extend fission studies down to elements of much lower atomic number. Table 1 indicates that the ellipticity² or permanent ground state distortion of nuclides again goes through a maximum in the heavy rare earth region. Since the expected fission cross sections

Table 1
Ellipticity Parameters for Selected Nuclides*

<u>Nuclide</u>	<u>Q/ZR^2</u>	<u>Compound Nucleus</u>	<u>Q/ZR^2</u>
$^{63}\text{Eu}^{151,153}$	0.050	$^{65}\text{Tb}^{155,157}$	0.063
$^{67}\text{Ho}^{165}$	0.079	$^{69}\text{Tm}^{169}$	0.099
$^{71}\text{Lu}^{175}$	0.126	$^{73}\text{Ta}^{179}$	0.115
$^{75}\text{Re}^{185,187}$	0.050	$^{77}\text{Ir}^{189,191}$	0.025
$^{79}\text{Au}^{197}$	0.013	$^{81}\text{Tl}^{201}$	0.003
$^{81}\text{Tl}^{203,205}$	0.003	$^{83}\text{Bi}^{207,209}$	-0.006
$^{82}\text{Pb}^{208}$	~ 0	$^{84}\text{Po}^{210}$	~ 0
$^{83}\text{Bi}^{209}$	-0.006	$^{85}\text{At}^{213}$	-0.012
$^{90}\text{Th}^{232}$	~ 0.05	$^{92}\text{U}^{238}$	~ 0.06

* Estimated from diagram in reference 2.

are extremely low (i.e. nanobarns); it would appear that even small effects on the fission barrier might be seen around $Z \approx 70$ from studies on neighboring nuclides.

The main problem in such studies is to prove that any observed fission is not due to some trace (p.p.b.) heavy element impurity. This is most easily accomplished by measuring enough of the fission mass yield curve to clearly differentiate the source of fission. Unfortunately, solid state devices are not presently capable of such differentiation at the expected low cross sections; however, radiochemical techniques appeared feasible.

Thick targets of highly purified Lu_2O_3 were prepared from oxidized lutetium solutions which had been passed through twenty feet of Dowex 50 cation exchange resin. Previous tests showed that it was possible to lower Th and U impurity levels to less than a few parts per trillion by this means. The bombarding energy of ~ 40 Mev was chosen since data on neighboring elements (Re, Au, Tl) were available at this same energy. Higher excitations would be expected to begin to mask the effect being sought and lower energies are not practical due to the rapid change of the fission cross section with energy.

The fission products that were removed from nineteen targets included As^{77} , Br^{82} , Br^{83} , Sr^{91} , Mo^{99} , Cd^{115} , I^{131} , I^{133} , and I^{135} . The results cannot be considered to be very accurate for a number of reasons, not the least of which is separating

a few cpm from 10^9 cpm of extraneous activities. However, the use of anti-coincidence guarded low-level counters (background = 0.14 cpm) and the efforts of the Argonne cyclotron crew to obtain high beam currents helped this problem a great deal. The most serious problem, however, is obtaining beam energy reproducibility from one bombardment to another. Even modest changes in the energy of the beam can introduce errors of the order of 50% in measured cross sections.

In spite of these difficulties, the relative cross sections³ (which are also equal to the thick target values) shown in Figure 1 are believed accurate enough for the purpose intended, indicating the source of fission to be a mass of approximately 170-190 ($\bar{\nu} = 1$). It should be noted that no Cd^{115} , I^{131} , I^{133} , or I^{135} could be detected until one target was deliberately "spiked" with 70 p.p.b. of Th^{232} . Further, the ratio of $\text{Br}^{82}/\text{Br}^{83}$ is very much larger for lutetium fission than for the corresponding heavy elements. The apparent "thick target" cross section for fission was estimated to be $1.25 \times 10^{-31} \text{ cm}^2$ by integration of the mass yield curve; it is corrected to a thin target value of $1.5 \times 10^{-30} \text{ cm}^2$ when suitable estimates are made for the change of cross section with energy.⁴ These estimates were based upon extensive studies of the helium-ion-induced fission of gold⁵ and similar research in these laboratories on rhenium.⁶

Figure 2 is a plot of a fission probability parameter, the fission to neutron width ratio, Γ_f/Γ_n vs. the fissionability term

Figure 1. Mass Yield Curve for Thick Target (Relative) Cross Sections for the Fission of Lu^{175} with 39.6 Mev Helium Ions.

Figure 2. Variation of Γ_f/Γ_n with Z^2/A (Compound Nucleus) at 36.3 Mev Excitation Energy.

Z^2/A for selected nuclides where the data are most complete. For the purposes of this discussion, Γ_f/Γ_n was taken as approximately equal to σ_f/σ_R for the lower Z elements. The data^{6,7,8} in Figure 2 are all for helium-ion-induced fission in the nuclides indicated at an excitation energy of 36.3 Mev. The present results are at least two orders of magnitude greater than would be expected by comparison with elements of higher Z having smaller permanent nuclear distortions.

If our interpretation of these data is correct, then fission studies on the lighter mass rare earths should show a decrease in the effect observed for lutetium. Unfortunately, the expected cross sections will be so small ($\sim 10^{-35}$ cm² for ${}_{67}\text{Ho}^{165}$) that proof of purity of the target material and measurement of the fission cross sections are only on the borderline of feasibility.

* This work was supported by the U. S. Atomic Energy Commission.

1. D. L. Hill and J. A. Wheeler, Phys. Rev. 89, 1102 (1953).
2. We have used the ellipticity factor as defined by R. D. Evans [The Atomic Nucleus, McGraw-Hill, New York, 1955, p. 172] equal to Q/ZR^2 , where Q is the quadrupole moment.
3. Total chain yield corrections were made using the CCR rule which was shown⁶ to be satisfactory for rhenium fission. In actual fact, the use of ECD or MNPE recipes does not make any difference in the estimated total cross sections within the large experimental errors involved. None of these corrections were over 10% except for Br^{82} .
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I. INTRODUCTION

Following the discovery of nuclear fission by Hahn and Strassman¹ in 1939, studies of the fission reaction have spanned almost the entire periodic table.^{2,3} The projectiles used have ranged from gamma rays to heavy ions; energies from essentially zero to a Bev or more. While such investigations have generally been concerned with gaining information about the fission reaction, they have also led to much of what is known today about nuclear properties. A survey of the review articles pertaining to nuclear fission³⁻⁹ indicates the wide scope of these studies and reveals the trends of experimental and theoretical investigations.

Most early studies were concerned with the fission of heavy elements of atomic number 90 or more induced by thermal or reactor neutrons. Modern nuclear technology is still primarily concerned with this area; however, any satisfactory theory of the nucleus must encompass the entire spectrum of nuclei and not just account for the observations in a limited region. Accordingly, there has been a growing interest in extending experimental studies of the fission reaction to nuclei of atomic number lower than those of the heavy elements. Admittedly, there have been many investigations of the fission of lower Z elements but these have almost always been of very high bombarding energies (often using heavy ions).

Under these conditions, it is doubtful that the reactions occurring are sufficiently similar to the low energy fission of the heavy elements to include them within a single framework.⁴ To allow direct comparison with the results of heavy element fission studies, the fission of lower Z elements must be performed at moderate excitation energies where the assumption of the compound nucleus concept is valid and where the fissioning nucleus can be more easily identified.

Investigations already performed in this region of low atomic number ($Z < 90$) have led to general agreement on some aspects of the fission reaction. There is little doubt that, for low Z nuclides, symmetric fission clearly predominates over the asymmetric fission which is characteristic of the fission of heavy elements ($Z \geq 90$) at moderate energies. Fairhall,¹⁰ Burnett,¹¹ and Vandenbosch and Huizenga¹² have found purely symmetric fission for $_{83}\text{Bi}^{209}$ as have Fairhall, Jensen, and Neuzil¹³ for separated $_{82}\text{Pb}$ isotopes. Brandhorst¹⁴ and Neuzil¹⁵ reported symmetric fission for $_{79}\text{Au}^{197}$ and Davis¹⁶ found $_{75}\text{Re}^{185,187}$ fission to be symmetric, supplanting earlier work by Griffioen¹⁷ which was thought to indicate some asymmetric fission for rhenium. Characteristic of low Z fission is the narrowness of the symmetric mass distribution in contrast to the much wider distribution for the symmetric fission of heavy elements.⁴ This observation lends support to the two-mode-of-fission hypothesis suggested by Turkevich and Niday¹⁸ and by Jensen and Fairhall¹⁹ which interprets the data to arise

from two separate types of fission. The asymmetric mode, relatively insensitive to excitation energy, predominates for heavy elements at moderate energy while for low Z elements only the extremely energy sensitive, symmetric mode is of significance. The triple-peaked fission of $_{88}\text{Ra}^{226}$ found by Fairhall and Jensen²⁰ and by Nobles and Leachman²¹ is thought to be due to approximately equal amounts of both modes of fission; a reasonable assumption since radium lies in the transition region between the heavy and the low Z elements. More recently, Sugihara, Roesmer, and Meadows²² have reported that they found about 0.3% asymmetric fission in the fission of bismuth with 36 Mev protons. Although the polonium compound nucleus formed is fairly far from the heavy elements, the very small amount of asymmetric fission found fits in satisfactorily with the generalizations drawn previously. In general, the two-mode-of-fission hypothesis has been substantiated, a recent example being the work of Britt, Wegner, and Gursky.²³

On the basis of the work cited, an investigation of the fission of lutetium would be expected to give a symmetric mass distribution. However, Halpern³ and Griffioen¹⁷ suggest that the purely symmetric fission around $_{82}\text{Pb}^{208}$ may be due to the effect of the doubly closed shells there and predict the possibility that asymmetric fission may become favored again for elements lying midway between the neutron closed shells of 82 and 126, lutetium being exactly half-way. In addition, Griffioen¹⁷ suggests that large deviations from spherical symmetry of the nucleus in the ground state as evidenced by a large quadrupole

moment might cause enhanced fissionability of that nucleus. The fission of lutetium would serve as a test for the validity of this prediction since it possesses an extremely large quadrupole moment.²⁴ Johansson,²⁵ considering the relationship between nuclear octupole deformation and the mechanism of fission, predicts that if asymmetry is to be found in low Z fission, it will be greatest around a Z of 72. Lutetium bombarded with helium ions would form a compound nucleus of Z equal to 73, close enough to investigate Johansson's suggestion.

The only fission studies reported in the rare earth region^{26,27} have used such high excitation energies (> 450 Mev) that the compound nucleus under consideration cannot be fixed nor can the exact reaction be determined. The proposed study of lutetium fission with roughly 40 Mev helium ions will involve fission very slightly above the threshold thus excluding any significant contribution by "second chance" fission and thereby avoiding confusion as to the identity of the fissioning nucleus.

Since the fissionability of nuclei of low Z decreases rapidly with decreasing Z, a study of the fission of lutetium would be expected to require experimental techniques and equipment of unprecedented sensitivity. In this laboratory, the capabilities for radiochemical fission studies have undergone considerable refinement as a consequence of previous investigations of the fission of gold,¹⁴ rhenium,^{16,17} and tantalum¹⁷ as well as the earlier work on heavy elements.²⁸⁻³⁸ It was of considerable interest to see if further extensions of experimental sensitivity

would permit a study of the fission of lutetium, a reaction anticipated to give extremely low cross sections (in the nanobarn region).

II. EXPERIMENTAL PROCEDURES

A. Preparation of the Lutetium

There are a number of considerations which make it essential to use lutetium of extremely high purity in the present attempt to induce fission in lutetium at lower energies. These are:

1) Extrapolation of the change of total fission cross section at a given energy with respect to decreasing atomic number of the target nuclide^{3,4,14-17} would lead one to expect individual cross sections of the order of nanobarns or even less in the fission of lutetium.

2) Lutetium, with an atomic weight of 175, would be expected to give a mass yield curve centered near mass 88 for helium-ion-induced fission; this region corresponds to the light fragment peak in the mass yield curves of heavy elements such as uranium and thorium.

3) Individual fission cross sections for heavy elements range up to as high as about 50 millibarns for helium-ion-induced fission around 40 Mev.

It is therefore evident that the fission products from even an extremely minute amount of heavy element impurity in the lutetium would mask those fission products likely to result from lutetium fission. Since the anticipated ratio of these cross sections is

of the order of 10^8 , it became necessary to purify the lutetium of heavy elements to less than one part in 10^{10} .

Preliminary experiments using radioactive tracers indicated ion exchange as one of the best means to achieve this level of purity. Full details of the purification will be reported elsewhere.³⁹

The lutetium solution obtained from the ion exchange columns was precipitated in the form of the hydroxide, $\text{Lu}(\text{OH})_3$. This precipitate was found to be mechanically unsuitable for cyclotron targets and was converted to the oxalate which was in turn ignited. The resultant Lu_2O_3 was then used directly for these fission studies. Only pure quartz or polyethylene labware was used in these steps to preclude the possibility of introducing heavy element impurities. Two separate batches of lutetium oxide were used in this study but as the experiments to prove its purity included both batches, it is certain that a standard and consistent purity was attained.

B. Target Preparation

While a metal foil is the ideal target material for cyclotron bombardments, this possibility was experimentally precluded in the case of lutetium. No means of preparing the metal consistent with the demands of purity were available and the oxide had to be used.

In view of the anticipated low cross section for lutetium fission, it was desirable to use the recently designed target holders previously reported by Davis¹⁸ (Figure 1). These target holders permit one to use a one-inch target. This has the benefit of

Figure 1. Photograph of the Target Holder Assembly Including a Target Plate and Cover Foils.

presenting a relatively larger area to the helium ion beam from the cyclotron and, consequently, higher beam currents can be focused on the target.

In order to use powdered Lu_2O_3 as a target material, a means had to be devised for proper mounting. Various trial runs resulted in the decision to use a grooved aluminum mounting plate ("target plate"). These target plates were machined from 40 mil (1 mil = 0.001 inch) aluminum sheets which had been rolled from a 99.9999% pure, zone-refined aluminum ingot.⁴⁰ Twelve equally spaced grooves were machined into a 1 1/8 inch square plate (Figure 1). Each groove was 30 mils wide and 25 mils deep with 10 mils spacing between grooves. Due to the burring tendencies of the ultra-pure, soft aluminum, these grooves were made somewhat U-shaped to facilitate machining. To remove any possible contaminants introduced by the lathe bit, each target plate was thoroughly washed in 6N HNO_3 in an ultrasonic cleaner. The target plates were reused for a number of targets following thorough washing in an ultrasonic cleaner three times each with 1N HCl , water, and ethanol.

The Lu_2O_3 powder was packed into the grooves of the target plates using a Lucite spatula. About 400 mg of Lu_2O_3 could be accommodated in the grooves of the whole target plate. A one mil aluminum foil was placed behind and in front of the target plate when mounting in the target holder. This aluminum foil was of 99.999% purity as analyzed by the supplier.⁴⁰

The assembled target was subjected to 70 pounds per square inch water pressure as a test to ensure that it would not rupture under the pressure of the cooling water during the bombardment. To prevent tearing of the front one-mil aluminum cover foil as a result of the stress of this water pressure, the target plate had previously been stressed under this pressure and would not flex during the pressure test. The front foil therefore was not stretched by the pressure test.

C. Cyclotron Bombardments

In view of the anticipated low cross sections, it was desirable to bombard with as high a helium ion current as possible for as long a time as was practical. The 60 inch cyclotron at Argonne National Laboratory was used for all bombardments in this research. The maximum external beam current for helium ions is of the order of 25 microamperes (μa) for this machine at the target position used.⁴¹ In practice, beam currents ranged from 5 to 25 μa . In all bombardments in this research, maximum beam currents were used. The beam current was continuously monitored and electronically integrated for all bombardments. The length of the bombardments ranged from 3 to 10 hours. For the short-lived activities of the order of two to three hours, longer bombardments do not have any further benefits.

At beam currents of 25 μa , the heat deposited in a target by a completely absorbed helium ion beam is of the order of 125

calories per second on an area of a few square millimeters. Even rhenium metal foils (melting point 3180°C and boiling point 5870°C ⁴²) have vaporized with beam currents of no more than $4\text{ }\mu\text{a}$.¹⁶ To avoid the temperature buildup probable in Lu_2O_3 with thermal conductivity a few orders of magnitude less than that of rhenium metal, improved target cooling was essential. As previously mentioned, the improved one-inch target holders were used (Figure 1). These holders are designed so that cooling water is passed forcibly over the immediate back side of the target rather than merely cooling the body of the holder. Also, the beam can be spread over a larger area thus reducing localized heating. With rhenium foil targets, these holders permitted cyclotron currents of $20\text{ }\mu\text{a}$ or more at 40 Mev .¹⁶

The feature of these target holders that makes them effective for cooling targets, namely, the circulation of water over the back of the target, has the unfortunate side effect of allowing the beam to penetrate into the water and induce radioactivity therein. Consequently, a completely separate closed-loop water cooling system had to be built and used. This system was in turn cooled by the cyclotron water cooling system but kept the radioactive water isolated. A block diagram of this additional system is shown in Figure 2. To prevent chemical attack on the target plate by impurities in the water, a one mil aluminum foil was placed behind the target plate in all of the bombardments. This foil was discarded after disassembly of each target, preventing

CYCLOTRON CONTROL ROOM

Figure 2. Diagram of the Auxiliary Cooling System for High Current Targets.

contamination of the target solution by radioactive impurities in the cooling water.

To ensure a diffuse beam and thus avoid "hot spots", a one mil duraluminum "stripping" foil located about 40 inches ahead of the target in the beam tube was used. Even with optimum focussing on this foil, the beam striking the target was spread over at least one square centimeter. In all of the targets, a seven-eighths inch (or smaller) aperture was used to restrict the beam to that area of the target which was occupied by the Lu_2O_3 .

An air flow over the target face is commonly used for cyclotron targets but a nitrogen flow was substituted in all targets in this study to prevent oxidation and consequent rupture of the front one mil aluminum cover foil. It was assumed that this foil was heated to high temperatures during the bombardments as it had only indirect cooling by the water.

The energy of the helium ion beam from the cyclotron was determined by absorption in aluminum to be 42.7 Mev based on the work of Bichsel, Mosley, and Aron.⁴³ Before the beam strikes the face of the Lu_2O_3 it passes in sequence through a one mil duraluminum foil to diffuse the beam, a similar foil to protect the cyclotron vacuum, a 7/8 inch nitrogen gap at atmospheric pressure, and a one mil aluminum foil covering the Lu_2O_3 . Therefore the beam incident on the Lu_2O_3 was 39.6 Mev. Standard considerations of conservation of momentum and of mass differences⁴⁴ relating to the Ta^{179} compound nucleus formed in the reaction

establish the excitation energy of these bombardments to be 36.3 Mev.

D. Chemical Procedures

The fission products isolated in this study, arsenic, bromine, strontium, and molybdenum, were selected for several reasons: 1) they have half-lives short enough to produce reasonable activity, yet long enough to permit extensive purification from contaminants; 2) they are all beta active thus permitting counting in low-level, anti-coincidence counters; 3) they do not require the analysis of complex mixtures of activities; and 4) their chemistry is reasonably well-defined.

In order to separate and purify a typical fission product with a few counts per minute from a target solution of 50 or more roentgens/hour, highly specific chemical procedures must be used. Since the fission products amount to only about 10^6 atoms, carrier techniques are necessary.

The target was dissolved in the presence of a known amount (about 20 mg each) of inactive carriers corresponding to those fission products which were to be removed. The element was then chemically separated and purified of all possible radioactive contaminants. Details of the procedures used are given in the appendix.

In view of the high levels of activity produced in these targets by spallation and neutron activation, it was necessary to

use the junior "hot cell" described by Davis¹⁵ for at least the initial chemical separations and purifications.

After purification, the element, in a suitable solid gravimetric form, was mounted on a counting planchet, weighed to determine the chemical yield, and its radioactive decay then followed in low-level background counters.

E. Counting Equipment

The development of extremely low background counters was a necessary prerequisite for this fission study in view of the very small (nanobarns) cross sections anticipated. Existing counting equipment in this laboratory had backgrounds of the order of one to two counts per minute (cpm) for beta counting. In order to detect a few cpm and follow the decay with even modest accuracy for several half-lives, considerably lower backgrounds were necessary.

Preliminary experiments were run with several different types of counting equipment to determine the possibility of their use for such low-level requirements. Gamma and beta-gamma coincidence methods were not satisfactory due to the high background to counting efficiency ratio even when operated inside massive shielding and in conjunction with a gas or a crystal "guard" anti-coincidence counter to electronically reduce background. Gas-flow beta counters operating in the Geiger region showed the most promise for low-level counting. A large number of counters of this type were constructed with varying design characteristics using a succession of different construction

materials to determine which was the least contaminated. These counters were all operated inside massive shielding using a large plastic scintillation crystal as a guard counter. Electronic anticoincidence circuits were utilized to cancel background counts occurring simultaneously in both detectors. As a result of these experiments, background was reduced to less than 0.5 cpm.

At this point, commercial low-level beta detectors became available and three model AC-1, 1 inch, Omni/Guard Beta Detectors were purchased from Tracerlab, Inc. of Boston, Massachusetts. These dual (sample and guard) detectors were guaranteed to have a background of less than 0.3 cpm if used with the proper type of counting system. The counters were incorporated into a complete counting system designed in this laboratory. They were housed in Lucite boxes 1) to furnish mechanical positioning, 2) to furnish some shielding for alpha and beta radiation from surrounding materials, and 3) to ensure that the counter would be surrounded by an atmosphere (counting gas) free of radon or other radioactive constituents of air. Machined steel sample tray assemblies were attached to the plastic boxes enabling the introduction and accurate positioning of the samples to be counted. These components were then encased in enclosures made of "ancient" steel, free of modern radioactive tracers. The steel enclosures served to furnish 1) shielding, 2) protection from light, and 3) a further enclosure for the desired counting gas atmosphere. Photographs of one of these counters and its enclosures are given in Figure 3. The three counter

Figure 3. Photographs of a) A Low-Level Dual Counter, b) The Counter in its Plastic Enclosure with Sample Tray Assembly Attached, and c) The Steel Enclosure Showing the Sample Tray Extended.

assemblies were placed adjacent to one another and surrounded on all sides by four inches of virgin lead with an additional four inches on the top. The design was such that after a period of operation, the entire atmosphere within the shielding would be counting gas. A commercially available gas mixture, 98.7% helium and 1.3% butane, was passed through each of the counters at a rate of $45 \text{ cm}^3/\text{minute}$.

Most of the associated electronics was designed and constructed in this laboratory.* Dual, regulated, RF, high voltage power supplies furnish the anode potentials. The net output signal from each of the solid state anticoincidence circuits is fed to an RIDL Model 49-26 transistorized scaler modified for this system. Upon reaching the preset count (any number from 1 to 10^6), a signal is fed to the control unit which in turn instructs the printer to print and the scaler to reset to zero and begin scaling again. The printers are of a dual type, one part being the time of day and the other being an elapsed time register, both pulsed by the "computer" unit. The elapsed time register records the length of the counting period accurate to one-tenth of a minute, resetting to zero after each print. A block diagram of the counting system is given in Figure 4.

With this triple, automated system it was possible to continuously count each of the samples from a target for any

* Design and construction by Edward Schmidlin of this laboratory.

Figure 4. Block diagram of the Low-Level Counting System.

length of time, consequently furnishing greatly improved counting data. A photograph of the complete system is shown in Figure 5.

These counters have backgrounds of 0.14, 0.15, and 0.15 cpm and have excellent stability and reliability. Activities could be followed to levels as low as even a few hundredths of a cpm for long counting periods. An example of the counting of an unusually low-level sample with this system is given in Figure 6.

F. Treatment of Data

The probability of formation of a given fission product nuclide can be expressed in terms of σ , the fission cross section, and may be calculated from the relationship:

$$\sigma = \frac{N}{n Q} . \quad (1)$$

N is the number of atoms of that fission product resulting from the bombardment of n target atoms per square centimeter by Q bombarding particles. In radiochemical fission studies σ is not, in general, determined for a single fission product nuclide. Instead, the cross section desired is the cross section for the formation of an isobaric sequence, i.e., a complete mass chain. Since the neutron-proton ratio of the primary fission products is approximately equal to the neutron-proton ratio of the compound nucleus, the primary fission products lie relatively far from the valley of stable nuclides and therefore rapidly decay by negatron emission along the series of isobars towards more stable nuclides. Due to the time required for chemical separation and purification, the activity of the very short-lived primary fission fragments

Figure 5. Photograph of the Low-Level Counting System.

Figure 6. A Measured, Low-Level Activity Counting Curve Showing its Computer-Analyzed Components.

cannot be determined but instead the activity of the isobars of convenient half-life of a few hours or more are counted. From the measured activity, the number of atoms of each nuclide present can be calculated. Any given member of the isobaric sequence which is determined will, in the usual case, only represent a certain fraction of the total formation probability of that mass chain. To determine the cross section for the entire isobaric chain, corrections for this fractional chain yield are necessary. In addition, corrections must be made for the growth and decay along the chain which has occurred during the bombardment and during the chemical manipulations before the sample is counted. Finally, corrections are necessary for the loss in yield of the nuclide during the chemical separation and purification and for the counting efficiency of the various counters.

In this fission study, the targets used were thick enough so that there was appreciable energy degradation of the beam between the face and the back of the Lu_2O_3 target material. Calculations were made of the range of helium ions in Lu_2O_3 based on the relationship⁴⁵

$$\frac{R_z + 0.01 Z/z}{R_{\text{air}}} = 0.90 + 0.0275Z + (0.06 - 0.0086Z) \log \frac{E}{M} \quad (2)$$

where R_z is the range in mg/cm^2 of a particle of mass M , energy E , and charge z in an element of atomic number Z ($Z > 10$). For the case of $3 \leq Z \leq 10$, replace $(0.90 + 0.0275Z)$ by 1.00. The usual assumption was made that the range of helium ions in a compound can be treated in terms of the ranges of helium ions

in the individual elements constituting the compound, i.e.,⁴⁵

$$\frac{1}{R_{\text{Lu}_2\text{O}_3}} = \frac{f_{\text{lutetium}}}{R_{\text{lutetium}}} + \frac{f_{\text{oxygen}}}{R_{\text{oxygen}}} . \quad (3)$$

R refers to the range in each of the indicated materials and f to the weight fraction of the elements in the compound. These calculations were made using a computer⁴⁶ and the resulting range-energy relationship is given in Figure 7. In a typical target of 100 mg/cm² thickness of Lu₂O₃, the beam is degraded about 9 Mev in traversing the target. Burnett⁴⁷ has calculated a theoretical fission barrier of over 35 Mev for lutetium, and Burnett et al.⁴⁸ have recently determined the excitation function for gold bombarded with helium ions. An extrapolation of the latter work to lutetium taking into account the high barrier has indicated that essentially all of the fission events would occur in the first few "Mev" of the target. Therefore n in equation (1), the number of lutetium atoms per square centimeter, loses significance since the situation is one of essentially an infinitely thick target. Straightforward calculations of σ for infinitely thick targets cannot be used since the excitation function is not known and certainly cannot be assumed to be constant or even linear over the experimental energy spread. Thus, initially, a constant (average) n was assumed and the calculated cross sections were assumed to be relative and not absolute. Further discussion of this will be found in Chapter IV.

The cross sections were calculated using the relationship

$$\sigma = \frac{A_0 C_1 C_2}{n Q \lambda f e} \quad (4)$$

Figure 7. Calculated Range of Helium Ions in Lutetium Oxide.

where σ = relative cross section in cm^2 ,

A_0 = activity at mid-time of bombardment (cpm),

n = target atoms per cm^2 ,

Q = total number of bombarding particles,

λ = decay constant (from Strominger et al.⁴⁹),

f = chemical yield fraction,

e = counter efficiency,

C_1 = correction factor for decay during bombardment,

and C_2 = CCR correction for independent yields.

The activity at zero time was determined by extrapolating the measured activity back to the mid-time of the bombardment according to the method proposed by Griffioen.¹⁷ The counting curves were plotted as usual on semi-log paper. Almost all of the empirical curves showed some contaminating activity but this was usually of low enough magnitude that graphical resolution of the curves yielded satisfactory data. The Los Alamos Pakag,^{50,51} a computer program able to resolve curves consisting of a sum of exponentials, was modified to help in this resolution.⁵² Most of the counting decay data were finally analyzed by this means. Figure 6 shows an experimental counting curve with two components as resolved by this computer technique.

The total number of bombarding particles, Q , was calculated from the integrated current measured for each bombardment. Since the machined dimensions of the target plates were such that 25% of the helium ion beam would be incident on the aluminum target plate itself and not on the Lu_2O_3 , the integrated currents measured were

reduced by that factor in the calculation of Q for each target.

The efficiencies, e , of the low level counters for the various isotopes used in this study were estimated by comparison with the counting efficiencies determined by Gunnink²⁸ for the usual Sugarman counters. Standards were used to determine the geometry factors for the low-level counters relative to the usual counters.

Calculations of cross sections are significantly simplified if they can be made using a relationship of the type of equation (1) or (4) rather than one which involves compensation for growth and decay during the bombardment. However, appreciable errors result from this simplification, particularly for short-lived isotopes, if the observed activity is extrapolated back to the end of the bombardment. Griffioen¹⁷ proposed that the simplified calculation can be used with little error if the observed activity is extrapolated exactly to the mid-time rather than to the end of the bombardment. He proposed a graphical solution which indicated that the error introduced is less than 1% for isotopes with half-lives greater than twice the length of the bombardment (i.e. $t_b/t_{1/2} < 0.5$). Davis¹⁶ extended this method to derive a universal curve which could be used to correct cross sections determined in this way for isotopes where $t_b/t_{1/2}$ became as high as two. Figure 8 shows a further extension of this correction for isotopes where $t_b/t_{1/2}$ is as large as five. The calculation

Figure 8. Cross Section Correction for Decay During Bombardment.

of this curve was based on the equation

$$\frac{\sigma_{\text{true}}}{\sigma_{\text{approx.}}} = \frac{\lambda t_b}{e^{\lambda t_b/2} - e^{-\lambda t_b/2}} \quad (5)$$

where λ is the decay constant for the isotope and t_b is the length of the bombardment. The ratio σ_T/σ_A is used directly as the correction factor C_1 in equation (4).

As indicated previously, the fission product nuclides which can be conveniently determined experimentally often represent only a fraction of the total fission products for that particular mass chain. The observed fraction may approach unity for nuclides which lie near the stable valley but can also be quite small, especially for nuclides which are "shielded" by stable or long-lived nuclides. The method used for correction of the experimental cross sections to yield the cross section for the entire mass chain has been the subject of considerable investigation and conjecture.^{4,32,53-57}

The postulate which has probably been most successful under the conditions of these fission experiments^{18,32,37} is known as the constant-charge-ratio (CCR) rule. The basic assumption of the CCR rule is that the most probable charge, Z_p , for a given fragment mass, A , is governed by the charge to mass ratio of the fissile nucleus, namely,

$$Z_p = \frac{A Z_c}{A_c - \bar{\nu}} \quad (6)$$

where Z_c and A_c are the charge and mass, respectively, of the compound nucleus and $\bar{\nu}$ is the average number of neutrons emitted in the fission. A graph of Z_p versus mass for various values of

$\bar{\nu}$ is given in Figure 9 for lutetium plus helium ions.

It has been experimentally determined that there is essentially a Gaussian distribution of charge probability symmetric about Z_p .^{4,32,57} The curve shown in Figure 10 of integrated fraction of chain yield versus ΔZ ($Z_{\text{fragment}} - Z_p$) as determined by Colby and Cobble³² was used for correcting the data in this study.

To determine $\bar{\nu}$, the average number of neutrons emitted in the fission, a value of $\bar{\nu}$ was first assumed and the CCR corrections were applied to the data accordingly. The resulting cross sections were then plotted on semi-log paper versus mass number. Each experimental point has a complementary point of the same magnitude determined by the relationship:

$$A_{\text{complementary}} = A_{\text{compound nucleus}} - \bar{\nu} - A_{\text{experimental}} \quad (7)$$

If both the experimental and the reflected data failed to fall on the same smooth curve, a different value of $\bar{\nu}$ was then assumed and the process repeated using the new, appropriate corrections. This procedure was repeated until the best, smooth, fission mass yield curve resulted; that corresponding value of $\bar{\nu}$ was then adopted.

Figure 9. CCR Lines of Most Probable Charge, Z_p , for $\text{Lu}^{175} + \text{He}^4$.

Figure 10. Integrated Fractional Chain Yield as a Function of Distance from Z_p , the Most Probable Charge.

III. EXPERIMENTAL RESULTS

The conditions under which each of the bombardments was made are given in Table 1. The length of each bombardment, t_b , and the integrated beam current, Q , were measured at the cyclotron during each run. Calculation of the total number of helium ions, Q , included the factor previously discussed pertaining to the fraction of the target area occupied by the Lu_2O_3 . The number of lutetium atoms per cm^2 , n , was calculated from the weight and area of the Lu_2O_3 . Where listed, cadmium and iodine were isolated in connection with proving the purity of the Lu_2O_3 , as will be discussed in the next chapter.

Tables 2 through 6 list the data and calculations for each of the isotopes studied. As previously discussed in connection with equation (4), A_0 is the extrapolated activity (cpm) at the mid-time of the bombardment, f is the fractional chemical yield, e is the counter efficiency, and C_1 is the correction for decay during the bombardment. The calculated cross sections, $\sigma_{\text{approximate}}$ (nanobarns), do not include C_2 of equation (4), the CCR correction for independent yields. The best value of $\sigma_{\text{approximate}}$ for each isotope, indicated below each table, is the value which was judged to be the most accurate. This evaluation was based both on the agreement of the data and on observations made during the experimental work which indicated the probable validity of the data.

In Table 7, the approximate cross sections have been corrected by the CCR rule for various values of $\bar{v}$, the average neutron boil-off, to give σ_{relative} , the cross section for formation of the complete mass chain.

The values of σ_{relative} for $\bar{v} = 1$ plotted against mass number are shown in Figure 11 with the best smooth curve drawn through both the experimental and the complementary reflected points.

Table 1
Bombardment data

<u>Tgt.</u>	<u>t_b(hr)</u>	<u>Q(μah)</u>	<u>Q(α's)</u>	<u>n(at/cm²)</u>	<u>Carriers isolated</u>
1	1.28	10.2	8.14x10 ¹⁶	2.64x10 ²⁰	Sr, Cd
2	3.18	30.6	25.1x10 ¹⁶	3.59x10 ²⁰	Sr, Cd
3	5.08	56.0	45.9x10 ¹⁶	3.22x10 ²⁰	Sr, Cd
4	4.88	57.1	48.1x10 ¹⁶	2.72x10 ²⁰	Sr, Zr, Cd, I
5	10.10	91.7	69.1x10 ¹⁶	2.73x10 ²⁰	Br, Sr, Cd, I
6	3.08	42.0	35.4x10 ¹⁶	3.62x10 ²⁰	Br, I
7	5.07	45.0	37.9x10 ¹⁶	3.70x10 ²⁰	Br, Sr, Cd, I
8	4.12	40.0	33.7x10 ¹⁶	2.98x10 ²⁰	Br, Sr
9	4.47	40.0	33.7x10 ¹⁶	3.02x10 ²⁰	Br, Sr
10	7.25	34.0	28.7x10 ¹⁶	3.12x10 ²⁰	Br, Sr
11	4.93	40.0	33.7x10 ¹⁶	3.29x10 ²⁰	Br, Sr
12	3.50	40.0	33.7x10 ¹⁶	3.13x10 ²⁰	Sr
13	6.53	60.0	50.6x10 ¹⁶	2.94x10 ²⁰	As, Mo
14	7.37	58.0	48.9x10 ¹⁶	3.04x10 ²⁰	As, Mo
15	8.00	50.0	42.2x10 ¹⁶	3.31x10 ²⁰	As, Mo
16	6.00	95.8	80.8x10 ¹⁶	3.13x10 ²⁰	As, Sr, Mo
17	7.50	44.8	37.8x10 ¹⁶	3.01x10 ²⁰	As, Sr, Mo
18	8.10	42.2	35.6x10 ¹⁶	3.48x10 ²⁰	As, Sr, Mo
19	8.93	82.0	69.1x10 ¹⁶	<u>3.64x10²⁰</u>	As, Sr, Mo

average: 3.17x10²⁰

Table 2

As⁷⁷ Data and Calculations

<u>Tgt.</u>	<u>A₀</u>	<u>f</u>	<u>e</u>	<u>C₁</u>	<u>σ_{app.}</u>	<u>Comments</u>
13	--	0	--	--	--	Lost in purification
14	--	0	--	--	--	Lost in purification
15	--	0	--	--	--	Lost in purification
16	--	0.101	--	--	--	Contaminated
17	--	0.072	--	--	--	Contam., cntrs. inoper.
18	3.17	0.112	0.318	0.999	2.66*	
19	53.7	0.225	0.354	0.999	10.4	

*Best value: $\sigma_{app.} = 2.66$ nanobarns

Table 3
Br⁸² Data and Calculations

<u>Tgt.</u>	<u>A₀</u>	<u>f</u>	<u>e</u>	<u>C₁</u>	<u>σ_{app.}</u>	<u>Comments</u>
5	2.87	0.365	0.292	0.998	0.38	Ag° on planchet
6	4.23	0.197	0.299	1.000	1.99*	
7	7.74	0.353	0.293	1.000	1.94*	Spiked with thorium
8	5.05	0.319	0.294	1.000	1.57*	
9	5.29	0.337	0.319	1.000	1.43*	
10	--	0	--	--	--	Lost in purification
11	5.21	0.385	0.291	1.000	1.36*	

*Best value: σ_{app.} = 1.66 nanobarns

Table 4

 Br^{83} Data and Calculations

<u>Tgt.</u>	<u>A₀</u>	<u>f</u>	<u>e</u>	<u>C₁</u>	<u>$\sigma_{\text{app.}}$</u>	<u>Comments</u>
5	472	0.365	0.376	0.717	2.34	Ag° on planchet
6	668	0.197	0.379	0.969	16.1*	
7	2529	0.353	0.378	0.915	30.0	Spiked with thorium
8	626	0.319	0.377	0.942	9.54*	
9	755	0.337	0.411	0.933	9.90*	
10	--	0	--	--	--	Lost in purification
11	1387	0.385	0.376	0.920	17.2*	

* Best value: $\sigma_{\text{app.}} = 13.2$ nanobarns

Table 5
 Sr^{91} Data and Calculations

<u>Tgt.</u>	<u>A₀</u>	<u>f</u>	<u>e</u>	<u>C₁</u>	<u>$\sigma_{\text{app.}}$</u>	<u>Comments</u>
1	--	0.214	--	--	--	Contaminated
2	--	0.105	--	--	--	Contaminated
3	--	0	--	--	--	Lost in purification
4	94.9	0.287	0.320	0.995	5.67	
5	81.3	0.143	0.407	0.979	5.25	
7	--	0	--	--	--	Lost in purification
8	--	0.055	--	--	--	Contam., cntr. inoper.
9	--	0	--	--	--	Lost in separation
10	0.86	0.018	0.403	0.989	1.08	
11	--	0.268	--	--	--	Contaminated
12	37.1	0.364	0.410	0.998	1.95	
16	272	0.172	0.407	0.992	12.6*	
17	--	0.439	--	--	--	Contaminated
18	34.4	0.404	0.377	0.986	1.66	
19	46.0	0.348	0.376	0.983	1.33	

* Best value: $\sigma_{\text{app.}} = 12.6$ nanobarns

Table 6

Mo⁹⁹ Data and Calculations

<u>Tgt.</u>	<u>A₀</u>	<u>f</u>	<u>e</u>	<u>C₁</u>	<u>σ_{app.}</u>	<u>Comments</u>
13	6.08	0.027	0.414	1.00	19.4	
14	4.30	0.111	0.413	1.00	3.46*	
15	0.67	0.070	0.413	1.00	0.99	
16	--	0.015	--	--	--	Counter inoperative
17	13.5	0.093	0.413	1.00	16.8	
18	3.50	0.109	0.413	1.00	3.94*	
19	11.6	0.204	0.414	1.00	3.58*	

* Best value: $\sigma_{app.} = 3.66$ nanobarns

Table 7

Cross sections corrected by CCR rule for total chain yield

<u>Iso.</u>	<u>σ_{app}</u>	<u>$\bar{\nu} = 0$</u>		<u>$\bar{\nu} = 1$</u>		<u>$\bar{\nu} = 2$</u>		<u>$\bar{\nu} = 3$</u>	
		<u>C_2</u>	<u>σ_{rel}</u>	<u>C_2</u>	<u>σ_{rel}</u>	<u>C_2</u>	<u>σ_{rel}</u>	<u>C_2</u>	<u>σ_{rel}</u>
As ⁷⁷	2.66	1.01	2.69	1.01	2.69	1.02	2.71	1.04	2.77
Br ⁸²	1.66	11.1	18.4	7.52	12.5	5.68	9.43	4.33	7.19
Br ⁸³	13.2	1.03	13.6	1.04	13.7	1.07	14.1	1.11	14.7
Sr ⁹¹	12.6	1.05	13.2	1.09	13.7	1.14	14.4	1.22	15.4
Mo ⁹⁹	3.66	1.01	3.70	1.01	3.70	1.02	3.73	1.05	3.84

All cross sections in nanobarns (10^{-33} cm^2)

Figure 11. Curve of Relative Cross Section versus Mass Number for the Fission of Lutetium (σ_{relative} defined in Chapter II, Section F).

IV. DISCUSSION

A. The Data and Experimental Errors

In a radiochemical fission study, the experimental errors are both those which are common to any analytical determination in the micro range and also those which are characteristic of radiochemical work. Among the latter should be included the standardization of carriers, the completeness of exchange between the radioactive isotope and the inactive carrier, counting efficiencies, resolution of complex decay curves, corrections for independent yield, and uncertainties in half-lives and decay schemes. Partly due to the extremely low levels of activity encountered in the present work, two additional sources of error were significant. These were the chemical purity and reproducibility of the samples being counted and the resolution of decay curves where unknown contaminants were also present. An estimation of the experimental error for each of the isotopes used in this study is given below.

As⁷⁷: The cross section calculated for this isotope was based on one of the two experimental points obtained (Table 2). The choice was made considering both the agreement with the data for the other mass numbers and considering the accurate determination made of the chemical yield for that one point by conversion to arsenic metal. In view of the use of just one point and due to

the complexity of the decay curve, the relative cross section calculated for mass 77 should be considered accurate only to a factor of two or three.

Br⁸²: The approximate cross section, $\sigma_{\text{approximate}}$, for this isotope is believed to be quite accurate, definitely within the usual $\pm 20\%$. All of the data is in good agreement except that from target number 5 (Table 3). It is quite certain that the error for that target is in f , the chemical yield, since the appearance of the precipitate corresponded to a yield of less than 10%. This lower yield would give a cross section in agreement with the other points. The correction for independent yield is very large in the case of Br⁸² (Table 7) since it is shielded by stable Se⁸². Consequently, although the experimental error in the relative cross section is estimated to be less than $\pm 20\%$, the overall error for this mass number depends greatly on the validity of the independent yield correction.

Br⁸³: With the exception of target 5, all the data agree fairly well (Table 4). The target 5 data also is in agreement if correction is made for the erroneous chemical yield, as discussed for Br⁸². Although the cross section found for target 7 is approximately twice that of the other targets, the thorium added to that target is responsible for the increase. If the contribution from the fission of thorium is subtracted, the net cross section is approximately the same as the assumed "best value." The overall error in the relative cross section is estimated to be $\pm 30\%$.

Sr^{91} : The counting data for strontium was easily resolved and is believed to be quite accurate but considerable difficulty was encountered in establishing the chemical yield of the strontium determinations. Flame photometry was used to check most of the yields but no significant errors were found for the determinations where useful counting data were obtained. Yet, it is believed that the lack of agreement of the data is a result of incorrect chemical yields. Others in this laboratory have, in general, reached the same conclusion. The probable errors in the chemical yields would raise the other values to some extent but since only the one determination was used in calculating the cross section, it should be considered as only a reasonable upper limit.

Mo^{99} : The counting data for molybdenum was easily resolved and the lack of agreement of the data is believed to be due to incorrect chemical yields and, perhaps, incomplete exchange of the Mo^{99} with the inactive carrier. It should be noted, however, that the data not included represent the smallest chemical yields and therefore have the greatest uncertainty in that respect. A colorimetric procedure (see Appendix) was used in an attempt to establish accurate chemical yields and, as a result, significant corrections were made to the initial gravimetric yields. The close agreement of the three determinations used to calculate the cross section lends support to the estimation of an accuracy of $\pm 30\%$.

The curve of relative cross section versus mass number

(Figure 11) is believed accurate to $\pm 30\%$. Most of the errors discussed for the individual points would not change the shape of the curve significantly and therefore this accuracy for the overall curve is not unreasonable.

B. Proof of Purity of the Lutetium

As indicated previously in Chapter II, section A, the validity of this fission study was dependent on the use of lutetium which was sufficiently free of heavy elements that there could be no doubt as to the source of the observed fission products.

The approach used to prove the purity of the lutetium was to search for fission fragments which are abundantly produced in known quantities in the fission of heavy elements (e.g., thorium and uranium) but which would be extremely unlikely products of the fission of lutetium. The isotopes selected were Cd^{115} , I^{131} , I^{133} , and I^{135} . In the fission of thorium and uranium induced by approximately 40 Mev helium ions, the cross sections for formation of these isotopes are from 30 to 40 millibarns.^{16,31} If these isotopes were to be fission products of lutetium, the corresponding mass split would be asymmetric with a mass ratio of about two to one. Such a mass-split ratio can be excluded by any reasonable considerations of the fission process. Therefore, any of these fission products found could be attributed to heavy element impurities in the lutetium.

In each of the first six targets, no activities were found

which could be identified as Cd^{115} , I^{131} , I^{133} , or I^{135} . From comparison of the measured activity (various contaminants of a few counts per minute or less) with hypothetical decay curves for these isotopes, an upper limit of less than a few parts per billion could be set for any heavy element impurities. Therefore, the contribution of heavy elements to the cross sections for lutetium fission were less than one percent. (A complete discussion of the preparation and proof of purity of the lutetium will be published elsewhere.³⁹)

As a check on the sensitivity of these determinations, seventy parts per billion of Th^{232} were added to one lutetium target (target number 7). From this target (and only this target), the activities of Cd^{115} , I^{131} , I^{133} , and I^{135} could easily be identified. The magnitude of the measured activities agreed closely with that expected from the fission of the added thorium.

Finally, a particularly definitive proof can be seen by inspection of the bromine isotope cross sections from the "spiked" target. Since Br^{82} is shielded by Se^{82} , a stable nuclide, all the Br^{82} observed must have been formed directly as a primary fission product. In the fission of heavy elements, the independent yield of Br^{82} is a very small part (2%) of the total yield for mass number 82. In the fission of lutetium, due to a lower neutron-to-proton ratio in the compound nucleus, the Z_p line falls considerably closer to Br^{82} and consequently the independent yield

of Br^{82} is much greater (about 13% of the chain of mass 82). Consequently, the addition of thorium to the lutetium target material should not change the cross section of Br^{82} appreciably, while that of Br^{83} should increase greatly, depending directly on how much thorium was added. The measured cross sections for the "spiked" target (number 7) show that the Br^{82} cross section was essentially the same as for the other targets while the cross section for Br^{83} is approximately twice that of the other, "unspiked" targets. Thus the experimental results bear out the expected effects of "spiking" the target with thorium.

In view of the results of these experiments, it appears certain that the cross sections determined should be attributed to the fission of lutetium and not to the fission of some heavy element impurity.

C. Estimation of the Absolute Cross Section

As discussed in Chapter II, section F, the cross sections calculated using equation (4) were relative and not absolute cross sections due to the use of thick targets. In order to have calculated the absolute cross sections from the thick target data at only one energy, some knowledge of the fission excitation function would have been necessary. Since this work is the first study of its type in this region of the periodic table, the excitation function was not known and therefore direct calculation of absolute cross sections was not possible.

In order to obtain an estimate of the absolute cross sections from the relative cross sections, an assumption must be made as to the nature of the fission excitation function for lutetium. Fission excitation functions have been published for many of the elements down to $Z = 79$ (gold). Of these, the work by Burnett et al.⁴⁸ on gold plus helium ions was the most applicable to this research. These authors determined the total fission cross section, σ_f , for excitation energies, E_{ex} , ranging from the fission barrier, about 22.5 Mev, to over 100 Mev. In this energy range, the total fission cross section varied from 10^{-35} cm^2 to 10^{-24} cm^2 . In view of the wide energy range of these experiments including measurements of σ_f at very low cross sections near the fission barrier and in view of the proximity of gold ($Z = 79$) to lutetium ($Z = 71$), it was decided to use the gold data to aid in estimating an excitation function for lutetium.

The experimental points of Burnett et al.⁴⁸ are plotted in Figure 12 with the energy coordinate representing the excitation energy, E_{ex} . An analysis of this data indicated that the excitation function near the fission barrier could be expressed in terms of a simple empirical relationship,

$$\sigma_f = k(E_{ex} - E_b)^5, \quad (8)$$

where E_b is the excitation energy at the fission barrier. Defining

$$\xi = E_{ex} - E_b, \quad (9)$$

equation (8) becomes

$$\sigma_f = k \xi^5, \quad (10)$$

Figure 12. Excitation Functions for the Fission of Gold Induced by Helium Ions. The Data Points are from Reference 48, Line A Gives σ_f versus ξ by Equation (10), and Curve B Shows σ_f versus E_{ex} by Equation (10).

where k is a constant for each particular fissioning nuclide, equal to 1.0×10^{-34} for the case of gold plus helium ions. In deriving this value for k , the same fission barrier height of 22.5 Mev was used as that reported by Burnett et al.⁴⁸ They determined this value for the fission barrier by a theoretical interpretation of their experimental data on the variation of cross section with energy. In Figure 12, line A indicates the variation of the fission cross section with ξ for gold and curve B gives the variation of the fission cross section with excitation energy, both curves being defined by equation (10). The fit of this simple empirical function to the gold data is quite good, particularly for energies less than 10 Mev above the barrier ($\xi < 10$ Mev), which is the main region of interest for application to the present work. A similar analysis was made on the data for Bi²⁰⁹ plus helium ions as reported by Huizenga, Chaudhry, and Vandenbosch,⁵⁸ assuming a reasonable value for the barrier energy, 17.0 Mev. Again, the data was well represented by equation (10).

In view of the success in representing such well-defined fission excitation functions by equation (10), it was assumed that that relationship would be applicable to the fission of lutetium as well.

Equation (1), page 20, can be written in a differential form as:

$$dN = \sigma_f Q dn \quad (11)$$

where N is the total number of fission products formed and σ_f is the total fission cross section. Since σ_f is a function of the energy (and therefore also of dn), it should be replaced by $k\xi^5$, from

equation (10). Multiplying by $d\xi/d\xi$, equation (11) becomes

$$dN = \frac{k \xi^5 Q dn d\xi}{d\xi} \quad (12)$$

The range-energy relationships, equations (2) and (3), define $dn/d\xi$ exactly but, for simplicity, $dn/d\xi$ can be assumed to be constant over a limited energy range (see Figure 7). Rearranging and integrating, equation (12) becomes

$$\frac{N d\xi}{Q dn} = \int_0^\xi k \xi^5 d\xi. \quad (13)$$

From equation (1), N/Q can be set equal to σn . σ is the total relative cross section, equal to one-half the area under the curve in Figure 11, and n is the number of target atoms used in calculating the cross sections in Figure 11. Thus the entire left hand side of equation (13) is known.

Since the fission barrier height for lutetium plus helium ions has not been determined, calculations were made for each of a series of reasonable barrier heights. Integrating equation (14) from 0 to ξ for E_{ex} equal to 36.3 Mev (Chapter II), the value of the constant, k , in equation (10) can be calculated for each value of E_b . The absolute total fission cross section can then in turn be calculated from equation (10). In Figure 13, the parallel straight lines give σ_f as a function of ξ for various values of the barrier energy, E_b . The straight line at E_{ex} equal to 36.3 Mev shows the variation in total fission cross section with the assumed barrier height for the present experimental work. The curved lines in Figure 13 give σ_f for various excitation energies and

Figure 13. Absolute Total Cross Sections Estimated for the Fission of Lutetium Induced by Helium Ions for Various Barrier Heights and Excitation Energies (from equation (10), p. 49, and equation (13), p. 52).

barrier heights as extrapolated from the present experimental work by these calculations.

Burnett and Thompson⁴⁷ have made semi-empirical liquid drop calculations of the fission barrier for a number of elements lighter than radium. These calculations indicate barriers of 25.61 Mev for gold and 35.43 Mev for lutetium. However, experimentally,⁴⁸ E_b was determined to be 22.5 ± 1.5 Mev. Assuming a constant percentage difference between the calculated and experimental values of E_b , the fission barrier energy for lutetium should be about 32 Mev. Hill and Wheeler,⁵⁹ in their theoretical discussion of fission in terms of the collective model of the nucleus, predict a lowering of the fission barrier for nuclides with large quadrupole moments. For the case of lutetium which has a very large quadrupole moment, the barrier energy may be lowered a few Mev. In view of these considerations, the most reasonable value of the fission barrier energy for lutetium plus helium ions is in the range of 29 to 32 Mev. From Figure 13, this leads to a total fission cross section of $(1.5 \pm 0.5) \times 10^{-30}$ cm² for lutetium at an excitation energy of 36.3 Mev.

D. Conclusions

The shape of the mass-yield curve for the fission of lutetium with 39.6 Mev helium ions is consistent with that observed in other fission studies in slightly higher Z regions of the periodic table. The curve is symmetrical with a full-width-at-half-maximum of 17.5 mass units, compatible with the data on rhenium¹⁶, gold^{14,15}, and

bismuth.¹⁰⁻¹² The average number of neutrons boiled off is approximately one, which is consistent with the trends observed in other, higher Z fission studies.

The constant-charge-ratio rule was used to correct for independent yields in this work, giving entirely satisfactory results. The equal-charge-displacement and minimum-nuclear-potential-energy rules were also used to estimate corrections to the data but the differences between these and the CCR corrections were less than the experimental errors involved. Consequently, no conclusions can be drawn as to the validity of either of these rules over the CCR rule.

In correlating the fission cross sections for various elements, it has been observed that there is an approximately linear relationship between $\ln (\Gamma_f/\Gamma_n)$ and the fissionability parameter, Z^2/A , at a given excitation energy. Such a correlation at 36.3 Mev excitation energy is shown in Figure 14 for elements of $Z \leq 83$, with ${}_{92}\text{Th}^{232}$ also shown as a typical heavy element. For the purposes of this correlation, the ratio of fission width to neutron emission width, Γ_f/Γ_n , can be assumed to be approximately equal to the ratio of fission cross section to total reaction cross section, σ_f/σ_R . The data used for the correlation in Figure 14 are given in Table 8. The Γ_f/Γ_n ratios for gold, thallium, lead, and bismuth were taken directly from the work of Huizenga, Chaudhry, and Vandenbosch.⁵⁸ For rhenium, the fission cross section at about 36.3 Mev reported by Davis¹⁶ was divided by the total reaction cross section at that energy calculated by Huizenga and Igo⁶⁰.

Figure 14. Ratio of Fission Width to Neutron Emission Width as a Function of Z^2/A at 36.3 Mev Excitation Energy.

Table 8

Ratio of Fission Width to Neutron Width for Selected Nuclides

<u>Nuclide</u>	<u>Z^2/A compd. nuc.</u>	<u>$\sigma_f(\text{cm}^2)$</u>	<u>$\sigma_R(\text{cm}^2)$</u>	<u>Γ_f/Γ_n</u>
$_{71}\text{Lu}^{175}$	29.8	1.5×10^{-30}	$1.8 \times 10^{-24}(\text{a})$	8.3×10^{-7}
$_{75}\text{Re}^{185, 187}$	31.2(b)	$5.6 \times 10^{-31}(\text{c})$	$1.8 \times 10^{-24}(\text{a})$	3.1×10^{-7}
$_{79}\text{Au}^{197}$	32.6			$5.0 \times 10^{-5}(\text{d})$
$_{81}\text{Tl}^{203, 205}$	33.0(b)			$2.0 \times 10^{-4}(\text{d})$
$_{82}\text{Pb}^{208}$	33.6			$1.0 \times 10^{-3}(\text{d})$
$_{83}\text{Bi}^{209}$	33.9			$6.7 \times 10^{-3}(\text{d})$
$_{90}\text{Th}^{232}$	35.8			$9.0 \times 10^{-1}(\text{c})$

(a) Interpolated from reference 60.

(b) Weighted for isotopic abundances.

(c) From reference 16.

(d) Estimated from diagram in reference 58.

(It is quite probable that the actual value of Γ_f/Γ_n is larger than that shown since Davis used thin target calculations even though his targets were too thick for this method of calculation. Correcting his data would raise the values of σ_f and Γ_f/Γ_n for rhenium.) In the case of thorium, the values of σ_f and σ_R given by Davis¹⁶ were extrapolated to 36.3 Mev. For lutetium, the absolute fission cross section calculated in section C was divided by a total reaction cross section interpolated from the work of Huizenga and Igo.⁶⁰ It is evident from Figure 14 that the fission cross section for lutetium is about two orders of magnitude greater than that expected by a simple linear extrapolation from the fission properties of higher Z elements.

The observed high fissionability of lutetium lends support to the prediction of Hill and Wheeler⁵⁹ that fission would be enhanced for a nucleus with a large quadrupole moment. Since the fission of a nucleus directly involves the distortion of that nucleus to the point where Coulombic repulsion overcomes nuclear force attraction, the ground state distortion associated with a large quadrupole moment can be considered, in effect, as contributing additional excitation energy to the nucleus. As a consequence, fissionability at a given excitation energy may be greater than expected from extrapolations from other nuclei which do not possess such large ground state distortions. This study of the fission of lutetium is the first real test of the effect of the quadrupole moment and its related ellipticity on the fissionability of a nucleus. The quadrupole moments of a large

number of nuclides have been measured. Evans²⁴ has correlated these observed quadrupole moments in terms of an ellipticity parameter, Q/ZR^2 , versus the number of odd nucleons in each nucleus and has found that there is a regular order, reaching maximum values about half-way between the so-called "magic numbers." In this parameter, Q is the observed quadrupole moment, Z is the nuclear charge, and R is the nuclear radius, here defined as $R = 1.5 \times 10^{-13} A^{1/3}$. The ellipticity of a nucleus can be calculated from the Q/ZR^2 parameter by the following relationship taken from Evans:⁶¹

$$\frac{Q}{ZR^2} \approx \frac{4}{5} \left(\frac{b}{a} - 1 \right) \quad (14)$$

where a and b are the major and minor axes of the elliptical nucleus. For the nuclei whose quadrupole moments have not been measured, the ellipticity parameter can be estimated from Evans' correlation. In Table 9, these ellipticity parameters are listed for each of the nuclides shown in Figure 14. Q/ZR^2 is given for both the target nucleus and for the compound nucleus formed with helium ions as the bombarding particles. It is evident from this table that of the nuclides with $Z \leq 83$, lutetium clearly has the most elliptical nucleus. But, more significant, of these nuclides, the ellipticity of the compound nucleus formed is extremely large only in the case of lutetium. Therefore, the effect of the quadrupole moment or ellipticity giving rise to increased fissionability would be expected to be greatest for lutetium among the nuclides of $Z \leq 83$ that have been studied. It should be pointed out that this effect may also be present in the fission of thorium and other heavy elements since they also have

Table 9

Ellipticity Parameters for Selected Nuclides*

<u>Nuclide</u>	<u>Q/ZR²</u>	<u>Compound Nucleus</u>	<u>Q/ZR²</u>
⁷¹ Lu ¹⁷⁵	0.126	⁷³ Ta ¹⁷⁹	0.115
⁷⁵ Re ^{185,187}	0.050	⁷⁷ Ir ^{189,191}	0.025
⁷⁹ Au ¹⁹⁷	0.013	⁸¹ Tl ²⁰¹	0.003
⁸¹ Tl ^{203,205}	0.003	⁸³ Bi ^{207,209}	-0.006
⁸² Pb ²⁰⁸	~ 0	⁸⁴ Po ²¹⁰	~ 0
⁸³ Bi ²⁰⁹	-0.006	⁸⁵ At ²¹³	-0.012
⁹⁰ Th ²³²	~-0.05	⁹² U ²³⁶	~ 0.06

* Estimated from diagram in reference 24.

large distortions. However, it would not be expected to be a significant effect in these heavy elements since they are extremely fissionable due to other reasons. Thus, the observed high fissionability of lutetium may bear out the prediction of Hill and Wheeler. However, to verify this conclusion, the fission of thulium ($Z = 69$) and other, lighter, rare earths should be studied. Thulium is estimated to have a quadrupole moment of about the same magnitude as lutetium and thus should show the effect to the same order of magnitude. However, as one proceeds to lighter nuclides, the effect of nuclear distortion on fission should diminish since the quadrupole moments and ellipticities again decrease in the lower rare earths. Therefore, a series of fission studies on the rare earths at constant excitation energy would provide additional and perhaps conclusive evidence on the prediction of Hill and Wheeler.

In order to fix more accurately the cross section for the fission of lutetium at these energies, a thorough experimental study should be made of the variation in cross section with energy using very thin targets. This research has demonstrated that such a study is now feasible. Indeed, it is not unreasonable to expect that fission studies can now be extended to elements of even lower atomic number. As Cohen and Swiatecki⁶¹ have pointed out, the fission of elements of $Z \leq 75$ is especially susceptible to theoretical treatment. The main problem lies in the experimental difficulties associated with the very small cross sections encountered in these elements. This research has shown that further studies of

fission in this region of Z are experimentally feasible and may have great significance in the definition of a satisfactory theory of nuclear fission.

V. SUMMARY

The results of this work on the fission of lutetium induced by helium ions can be summarized as follows:

1) This research has experimentally demonstrated the presence of fission in lutetium at low excitation energy.

2) The mass yield curve at an excitation energy of 36.3 Mev is symmetric about mass 89 with a full-width-at-half-maximum of about 17.5 mass units. It appears that an average of one neutron is emitted per fission event.

3) The total fission cross section at 36.3 Mev is estimated to be 1.5 ± 0.5 microbarns.

4) The enhanced fissionability of lutetium compared to other (higher Z) elements is attributed to the significant ground state distortion of the fissioning nucleus as indicated by its large quadrupole moment.

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APPENDIX

SEPARATION AND PURIFICATION CHEMISTRY

This appendix is divided into two sections, the first dealing with the chemical procedures necessary to separate the desired fission products from one another while the second section concerns the procedures necessary to ensure satisfactory radioactive purification of the separated fission products from all other possible contaminants.

These procedures are, for the most part, standard radiochemical procedures modified for rare earth fission studies. For reference, previously published sources should be consulted.^{1,2,3,4}

A large number of details are given in the following pages, mainly as a guide to aid in future research which may involve similar problems in the attainment of extremely high purification levels.

I. Separation Chemistry

A diagram of the separation of those fission products studied in this research is summarized in Figure 1. Arsenic, bromine, strontium, and molybdenum were used to investigate the fission of lutetium while cadmium and iodine were used as monitors in the proof of purity of the lutetium with respect to heavy elements.⁵ Paragraphs B through G refer to the separation

Figure 1. Flow Diagram of the Chemical Separations.

of bromine, strontium, cadmium, and iodine and paragraphs H through M to the separation of arsenic, strontium and molybdenum. These are given as separate procedures because they involve incompatible conditions such as oxidizing media and because they were, in fact, developed as distinct procedures.

A. Target Disassembly

Disassemble the target holder using a fitted brass shield to facilitate rapid removal of the hold-down screws as well as to provide some radiation shielding. Remove the one mil aluminum front and rear cover foils from the target plate. Place the target plate in a 30 ml beaker containing about 20 mg each of the standardized carriers (Table 1).

B. Target Dissolution

Using a stream of water, wash as much as possible of the lutetium oxide out of the grooved target plate. Add about 1 ml of conc. HCl and, if necessary, further water to cover the target plate. Place the beaker in an ultrasonic bath for a few seconds. Remove the target plate from the solution, rinsing it thoroughly with water. Place the beaker and contents on a hot plate in the radiation "hot cell" and add a glass bead. Add a few ml of conc. HCl and heat to gentle boiling. Continue adding HCl as the solution process proceeds until all the lutetium oxide is dissolved (about 30 minutes.)

Table 1. Special Reagents

Arsenic carrier:	10.07 mg As/ml as As_2O_3
Bromine carrier:	11.04 mg Br/ml as NaBr
Strontium carrier:	10.54 mg Sr/ml as SrCl_2
Molybdenum carrier:	15.10 mg Mo/ml as H_2MoO_4
Saturated CCl_4 :	Saturate CCl_4 with Cl_2 gas, wash free of excess Cl_2 with dilute NaOH.
Magnesia mixture ^{8,9} :	50 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ + 70 g NH_4Cl + 400 ml H_2O + 100 ml 15M NH_4OH . Dilute 1:1. Filter.
Conc. NH_4OH :	Pass NH_3 gas through conductivity water until saturated.
Conc. HCl:	Pass HCl gas through conductivity water until saturated.

C. Precipitation of Lutetium Hydroxide

Transfer the target solution to a 40 ml centrifuge cone, dilute to about 20 ml, and carefully add conc. NH_4OH dropwise to give a pH of about 5. Note carefully: Because $\text{Sr}(\text{OH})_2$ will form if a small region of pH 11 occurs and will not redissolve unless the pH is lowered to below 3, it is important to stir vigorously as the NH_4OH is added. Centrifuge the $\text{Lu}(\text{OH})_3$ precipitate and decant. The decantate, containing all of the carriers, usually will have very low activity after this precipitation.

D. Extraction of Iodine

Place the decantate from the $\text{Lu}(\text{OH})_3$ precipitation in a separatory funnel and acidify with 1 to 2 ml of 6N H_2SO_4 . Add 5 ml of CCl_4 (to avoid possible loss of bromine in the following separation to unsaturated CCl_4 , use CCl_4 which has been saturated with gaseous Cl_2 and then washed free of Cl_2 with dilute NaOH). Add one drop of 1M NaNO_2 , shake well, and collect the organic layer in another separatory funnel. Check for complete extraction with more CCl_4 and NaNO_2 and repeat as necessary.

E. Extraction of Bromine

Place the aqueous solution remaining from the iodine extraction in another separatory funnel, add 1 ml of 6N H_2SO_4 , 5 ml of saturated CCl_4 , and 1/2 ml of chlorine water. Shake well and then drain off the CCl_4 layer into another separatory funnel. Repeat this extraction procedure until essentially all of the bromine has been extracted.

F. Precipitation of Cadmium Sulfide

Add conc. HCl dropwise to the aqueous solution remaining after the extraction of bromine to give a pH of 5 and saturate the solution with H_2S . Centrifuge the CdS precipitate and decant, saving the decantate for strontium.

G. Precipitation of Strontium Carbonate

To the decantate from the CdS precipitation, add a few drops of conc. HCl and boil the solution to remove dissolved H_2S . Add conc. NH_4OH dropwise to give a pH of 8. Add 5 ml of saturated Na_2CO_3 , digest at 85° for a few minutes, cool, centrifuge the SrCO_3 precipitate and decant, discarding the decantate.

H. Target Dissolution

Using a stream of water, wash as much as possible of the lutetium oxide out of the target plate. Add about 1 ml of conc. HCl and enough water to cover the target plate. Place the beaker in the ultrasonic bath for a few seconds. Remove the target plate from the solution, washing it off thoroughly with water. Place the beaker on a hot plate in the hot cell and add a glass bead. Add a few ml of conc. HCl and a few drops of 30% H_2O_2 and heat to gentle boiling. Continue adding HCl and H_2O_2 as the solution process proceeds until all of the lutetium oxide is dissolved (about 30 minutes). The peroxide is necessary to maintain arsenic in the pentavalent state and therefore prevent its volatilization as AsCl_3 .

I. Precipitation of Arsenic and Molybdenum Sulfides

Transfer the target solution to a centrifuge cone and add conc. NH_4OH dropwise until the solution is estimated to be about 1N in HCl by noting the relative volumes. Add a few crystals of NH_4I to catalyze the reduction of As(V) to As(III) and bubble H_2S through the solution for a few minutes. Centrifuge and decant (digestion at 85°C for a few minutes may be necessary to ensure a clean separation of the sulfides). The decantate will contain strontium and most of the lutetium.

J. Precipitation of Lutetium Hydroxide

Boil the decantate from above (or digest at high temperature) to remove the dissolved H_2S . Add conc. NH_4OH dropwise to give a pH of about 5. All the lutetium should precipitate as $\text{Lu}(\text{OH})_3$ at this pH. Note carefully: $\text{Sr}(\text{OH})_2$ will form at a pH of about 11 and will not redissolve until the pH is lowered to below 3. Therefore, stir vigorously when adding the NH_4OH to prevent regions of abnormally high pH. Centrifuge and decant, discarding the $\text{Lu}(\text{OH})_3$ precipitate which is responsible for most of the target radioactivity.

K. Precipitation of Strontium Carbonate

To the decantate containing strontium, add conc. NH_4OH dropwise to give a pH of 8. Add 5 ml of saturated Na_2CO_3 to precipitate SrCO_3 . Digest at 85°C for a few minutes, cool, centrifuge and decant, discarding the decantate.

L. Precipitation of Molybdenum Oximate

Wash the mixed arsenic and molybdenum sulfides with a few ml of hot water, centrifuge and decant, discarding the decantate. This will remove some of the remaining lutetium activity. Add about 5 ml of conc. NH_4OH to the precipitate, heat to about 90°C , and add 30% H_2O_2 dropwise to dissolve the sulfides. (Care must be used in adding the H_2O_2 as the reaction is quite vigorous.) Some $\text{Lu}(\text{OH})_3$ may form in this basic solution. If so, centrifuge and decant, discarding the precipitate. Adjust the volume to 15 to 20 ml, add conc. HCl until the solution is estimated to be about 1N in HCl and then add at least 5 ml of alcoholic 2% α -benzoin oxime solution to form the voluminous molybdenum oximate. Centrifuge and decant, checking the decantate with a few ml of α -benzoin oxime to ensure complete precipitation of the molybdenum. Save the decantate which contains the arsenic.

M. Precipitation of Arsenic Sulfide

To the decantate from the molybdenum oximate precipitation, add a few crystals of NH_4I . Bubble H_2S through the solution for a few minutes, centrifuge and decant, discarding the decantate. If the resulting As_2S_3 cannot be centrifuged cleanly, digestion at 85°C for a few minutes followed by standing in an ice bath for a few minutes will usually hasten the coagulation. If As_2S_3 floats on the surface of the supernatant, wet it with 95% ethanol, carefully layer 2 to 3 ml of diethyl ether on top of the alcohol, centrifuge and decant, discarding the decantate.

II. Purification Chemistry

A. Arsenic

The basic steps used in the purification of arsenic were selective precipitations as magnesium ammonium arsenate and arsenic sulfide, distillation as arsenic trichloride, and reduction to metallic arsenic (Figure 2). Each of these steps was performed at least twice to reduce the contamination of the sample. La^{+3} carrier was added at various points in the procedure to act as a hold-back carrier for the rare earths including lutetium.

Arsenic was mounted for counting as magnesium ammonium arsenate. The precipitate was washed three times each with 5 ml of water, ethanol, and diethyl ether, transferred to a weighed planchet, dried at 110°C for 30 minutes, cooled, and weighed as $\text{MgNH}_4\text{AsO}_4 \cdot 1/2 \text{H}_2\text{O}$ (39.37% As).

Seven separate attempts were made to isolate arsenic from targets of which only the last two were successful. The remaining five attempts were probably unsuccessful due to the precipitation of lutetium arsenate in basic solution and subsequent loss as arsine during recovery attempts using strong reducing conditions. Some difficulty was encountered with the final $\text{MgNH}_4\text{AsO}_4$ precipitation. It was found that coprecipitation of some unknown compound was avoided only if this final step were preceded by a sulfide precipitation. Chemical yields were in the range of 10 to 25 per cent. Recycling through all of the chemistry steps of an aliquot of one of the arsenic samples resulted in a proof of

SULFIDE PRECIPITATION

MAGNESIUM AMMONIUM
ARSENATE PRECIPITATION DISTILLATION OF AsCl_3

REDUCTION TO As METAL

Figure 2. Flow Diagrams of the Purification of Arsenic.

constant specific activity for that sample.

1) Precipitation of Magnesium Ammonium Arsenate. Neutralize the arsenic solution with conc. NH_4OH added dropwise and then add a volume of conc. NH_4OH equal to one-third the volume of the solution. Add 5 ml of magnesia mixture (Table 1), digest for 5 minutes, cool to room temperature, centrifuge and decant, discarding the decantate. Dissolve the $\text{MgNH}_4\text{AsO}_4$ in 1 ml of conc. HCl .

2) Precipitation of Arsenic Trisulfide. Add a few crystals of NH_4I to the arsenic solution in order to catalyze the reduction of As(V) to As(III) . Place the centrifuge cone in an ice bath and pass H_2S through the solution until a yellow precipitate is formed. Centrifuge and decant, discarding the decantate. (If the sulfide is semi-colloidal, digestion for a few minutes will usually hasten coagulation.) Dissolve the As_2S_3 in 1 ml of conc. HNO_3 and add a few drops of 30% H_2O_2 with heating. To destroy excess peroxide, boil the solution briefly.

3) Distillation of Arsenic Trichloride. Set up an all glass distillation apparatus with provision for passing a carrier gas through the solution and for the addition of reagents without having to take apart the apparatus. To the flask add the arsenic solution, a few glass beads, appropriate carriers, and 10 ml of conc. HCl . Place a centrifuge cone surrounded by an ice bath so that the tip of the delivery tube is near the bottom of the cone. Add 5 ml of 30% H_2O_2 to the distillation flask and start a flow of HCl gas through the still at a rate of about 2 to 3 bubbles per

second. Add 10 ml of water to the collector cone. Distill the contents of the flask to one-half of the volume. Stop the HCl flow, add 2 ml of 30% H_2O_2 , thoroughly rinse the reagent funnel with water (to prevent violent reaction later with HBr), and restart the HCl flow. Distill until only a few ml remain. Remove the collector cone and discard, stop the flow of HCl gas, place a new iced collector cone in position, add 10 ml of 40% HBr to the flask, restart the HCl flow, and add 10 ml of water to the collector cone. Distill until only a few ml remain. Repeat the distillation with another 10 ml of 40% HBr and another collector cone (usually all the arsenic will be found in the first cone). Since the As(III) is now in a strong HCl medium, reduction to the metal is a convenient next step.

4) Reduction to Metallic Arsenic. Adjust, if necessary, the arsenic solution to at least 6N in HCl, add 1 g of sodium hypophosphite, and digest at 85°C with frequent stirring until black arsenic metal has formed and coagulated. Centrifuge and decant, discarding the decantate. (To precipitate arsenic floating on the surface, wet with ethanol, cover with a layer of diethyl ether, and centrifuge.) Dissolve the precipitate in 2 ml of conc. HCl and a few drops of 30% H_2O_2 with heating. To destroy excess peroxide, boil the solution briefly.

B. Bromine

Solvent extraction and distillation were the two basic steps used in the purification of bromine (Figure 3). The solvent extrac-

CARBON TETRACHLORIDE EXTRACTION

IODINE SCAVENGE

DISTILLATION

Figure 3. Flow Diagrams of the Purification of Bromine.

tion was performed from two to eight times and the distillation at least twice. Scavenge steps were performed for iodine after every extraction except the one immediately preceeding mounting.

La^{+3} was added at various points as a hold-back carrier.

Bromine was mounted for counting as silver bromide. A few ml of 0.1M AgNO_3 were used to precipitate the bromide from a solution which had been heated to destroy any excess bisulfite from the previous purification steps. Care was taken to prevent exposure of the AgBr precipitate to light and to use only aluminum planchets which had smooth surfaces (a scratched surface apparently catalyzes decomposition of AgBr). The AgBr was washed three times each with 5 ml of water, ethanol, and diethyl ether, transferred to a weighed planchet, dried at 110°C for 10 minutes, cooled and weighed as AgBr (42.55% Br).

Six attempts to recover bromine were made of which all but one were successful. Chemical yields ranged from 20 to 40 per cent. In one case, it appeared that metallic silver on the planchet caused an incorrect (high) chemical yield and hence an erroneously low cross section.

1) Carbon Tetrachloride Extraction. To the aqueous bromide solution in a separatory funnel add 2 ml of conc. H_2SO_4 and 5 ml of saturated CCl_4 (see Table 1). Add 0.1M KMnO_4 dropwise with shaking until the permanganate color persists in the aqueous layer. Drain the organic layer into another separatory funnel. Check for complete extraction with more CCl_4 and KMnO_4 and repeat as necessary. To the

combined organic phases, add 5 ml of water, a few drops of 6N H_2SO_4 and a few drops of 1M NaHSO_3 and shake well until both phases are colorless. Add more NaHSO_3 if necessary. Discard the organic layer.

2) Iodine Scavenge. To the aqueous bromide solution in a separatory funnel add 5 mg of iodine carrier and 5 ml of saturated CCl_4 . Add one drop of 1M NaNO_2 , shake, and discard the colored organic layer. Repeat as necessary to completely remove the iodine.

3) Distillation. Place the aqueous bromide solution in a distilling flask fitted to allow a flow of air as a carrier gas for the bromine. Place a collector cone containing 30 ml of water and 1 ml of 1M NaHSO_3 so that the delivery tube extends nearly to the bottom of the cone. Add 2 ml of chlorine water (or 0.1M KMnO_4) to the distilling flask, start a slow flow of air, and heat the flask gently. Check for completeness with another 1 ml of chlorine water. Remove and heat the collector cone to near boiling to destroy the excess bisulfite.

C. Strontium

The basic steps used in strontium purification were carbonate, nitrate, and oxalate precipitations, and barium and yttrium scavenges (Figure 4). In order to remove essentially all radioactive contaminants, each of the precipitations was performed at least three times and each of the scavenge steps at least twice. Frequently, lanthanum carrier was added, either

OXALATE PRECIPITATION

CARBONATE PRECIPITATION

NITRATE PRECIPITATION

BARIUM SCAVENGE

YTTRIUM SCAVENGE

Figure 4. Flow Diagrams of the Purification of Strontium.

as a hold-back carrier for the rare earths in nitrate precipitations or as a rare earth scavenge along with an yttrium scavenge.

Strontium was mounted for counting as the oxalate. The final oxalate precipitate was washed three times each with 5 ml of water, ethanol, and diethyl ether. The strontium oxalate was then transferred to a weighed planchet, dried at 300°C for 15 minutes, cooled, and weighed as SrC_2O_4 (49.89% Sr).

A total of fourteen attempts were made to isolate strontium of which seven were successful. The remainder were either of negligible chemical yield or contaminated. It is believed that those of negligible yield were the result of the presence of silicates in the NH_4OH and consequent loss of strontium as the completely insoluble strontium silicate. For this reason, NH_4OH made from gaseous NH_3 is highly recommended (Table 1).

The barium chromate scavenge was found to be particularly effective in removing contamination but careful control of the pH is necessary. A low pH results in only partial precipitation of the barium while a high pH results in strontium chromate coprecipitation and thus a greatly reduced chemical yield. Further, if the barium is not completely removed as the chromate, it will follow the strontium chemistry and give an incorrect (high) chemical yield for strontium. Most of the strontium samples were analyzed by flame spectrophotometry as a check for chemical purity.*

* The cooperation of Professor G. E. Wilcox of the Department of Horticulture is gratefully acknowledged.

About one-half were found to be impure but these were also the radioactively contaminated samples and thus no corrections to calculated cross sections were necessary.

1) Oxalate Precipitation. To the strontium solution, add conc. NH_4OH dropwise to give a pH of 8 or 9. Add 5 ml of saturated $(\text{NH}_4)_2\text{C}_2\text{O}_4$, stir, and digest at 85°C for 5 minutes. Cool to room temperature, centrifuge and decant, discarding the decantate. Wash the precipitate with 5 ml of water and 1 ml of saturated $(\text{NH}_4)_2\text{C}_2\text{O}_4$, centrifuge and decant, again discarding the decantate. Dissolve the precipitate in 0.5 ml of conc. HCl and a few drops of 30% H_2O_2 to decompose the oxalate and then heat to boiling to destroy excess peroxide.

2) Nitrate Precipitation. Carefully add 3 or 4 volumes of fuming nitric acid to the strontium solution (70% nitric acid concentration is necessary for quantitative precipitation³). Cool at ice temperature for 5 minutes, centrifuge and decant, discarding the decantate into a special container for waste concentrated nitric acid. Dissolve the $\text{Sr}(\text{NO}_3)_2$ in a few ml of water.

3) Carbonate Precipitation. To the strontium solution, add conc. NH_4OH dropwise to give a pH of 8. Add 5 ml of saturated Na_2CO_3 solution, stir, and digest at 85°C for 5 minutes. Cool to room temperature, centrifuge and decant, discarding the decantate. Wash the precipitate with 5 ml of water and 1 ml of saturated Na_2CO_3 , centrifuge and decant, discarding the decantate. Dissolve the resulting SrCO_3 precipitate with a few drops of conc. HCl and then add a few ml of water.

4) Barium Chromate Scavenge. To the strontium solution, add 5 mg of Ba^{+2} carrier, neutralize the solution with conc. NH_4OH , add 1 ml of 6M $\text{HC}_2\text{H}_3\text{O}_2$ and 2 ml of 6M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, heat the solution to boiling, and add 3 ml of 1.5M K_2CrO_4 . Digest at 85°C for 10 minutes with occasional stirring, centrifuge and decant, saving the decantate and discarding the precipitate.

5) Yttrium Hydroxide Scavenge. Add 5 mg of yttrium carrier to the strontium solution, heat to nearly boiling, and add conc. NH_4OH dropwise to give a pH of 9. Digest at 85°C for 5 minutes with occasional stirring, centrifuge and decant, saving the decantate and discarding the precipitate. If corrections for yttrium grow-in while counting will be appreciable, note the time of the scavenge.

D. Molybdenum*

The basic steps used in the purification of molybdenum were precipitation as the oximate followed by a ferric hydroxide scavenge (Figure 5). It was necessary to repeat these steps in sequence five or six times to reduce contaminants to an acceptable level.

Molybdenum was mounted for counting as silver molybdate (see 3) below and Figure 5). The precipitate was washed twice each with 5 ml of ethanol and diethyl ether, transferred to a weighed planchet, dried at 110°C for 15 minutes, cooled, and weighed as Ag_2MoO_4 (25.54% Mo).

Six of the seven attempts to isolate molybdenum were success-

*The assistance of R. H. Iyer is gratefully acknowledged.

OXIMATE PRECIPITATION

SILVER MOLYBDATE PRECIPITATION

FERRIC HYDROXIDE SCAVENGE

Figure 5. Flow Diagrams of the Purification and Mounting of Molybdenum.

ful. Chemical yields ranged from 3 to 20 per cent. The chemical purity of all the samples was checked by a standard colorimetric method⁶ using a Cary Spectrophotometer with the result that corrections of 25 to 50 per cent were made to the previous gravimetric yields. The need for these corrections, as well as similar observations by others,⁷ indicates that the silver molybdate procedure is not entirely satisfactory. Lead molybdate has been suggested as a better gravimetric precipitate.⁷

1) Molybdenum Oximate Precipitation. Add conc. HCl to the molybdenum solution so that the concentration is estimated to be about 1N in HCl. Add 5 to 10 ml of 2% α -benzoin oxime in alcohol, stir well, and cool at ice temperature for 5 minutes. Centrifuge and decant, discarding the decantate. Thoroughly wash the precipitate with 30 ml of 0.5M HCl. Centrifuge and decant, discarding the decantate. Repeat the washing.

Add about 2 ml of conc. HNO_3 to the molybdenum oximate precipitate to make a slurry and then transfer it to a 100 ml Erlenmeyer flask. Dissolve the precipitate with gentle heating. Add about 1 ml of 70% HClO_4 and cautiously heat the solution to dryness over a flame. (Note carefully: Use the utmost of care as this is a violently explosive mixture. Work behind a shield with gloved hands and tongs. Due to the use of extreme care, this step has been without incident as yet.) Allow the residue to cool, add about 2 ml of conc. NH_4OH to dissolve it, and transfer the solution to a centrifuge cone.

2) Ferric Hydroxide Scavenge. Dilute the molybdenum solution to about 20 ml with water and make it slightly acidic with conc. HCl. Add about 3 mg of ferric chloride carrier and then add conc. NH_4OH slightly in excess to precipitate ferric hydroxide. Stir well, centrifuge and decant, discarding the precipitate after decanting into another centrifuge cone. Repeat, using 2 mg of ferric carrier.

3) Silver Molybdate Precipitation for Mounting. To the molybdenum solution from the oximate precipitation, add water to make a total volume of about 20 ml. Add 6M HNO_3 to make the solution slightly acidic (chloride ion must be avoided). Add 3 mg of ferric nitrate carrier and then conc. NH_4OH slightly in excess to precipitate $\text{Fe}(\text{OH})_3$. Centrifuge and decant, discarding the precipitate. To the decantate, add a drop of methyl red indicator and make the solution slightly acidic with 6M HNO_3 . Boil briefly and then add 2 ml of 10% sodium acetate followed by 1 ml of 1M AgNO_3 added dropwise. Stir well and cool to room temperature. Centrifuge and decant, discarding the decantate.

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VITA

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