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UNITED STATES ATOMIC ENERGY COMMISSION

PRODUCTION AND SEPARATION OF U^{233}

Collected Papers

Edited by
Leonard I. Katzin

1952

Argonne National Laboratory
Lemont, Illinois

Technical Information Service Extension, Oak Ridge, Tenn.

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I

PRODUCTION AND SEPARATION OF U^{233}

Collected Papers

TID-5223 (Pt. I)

Edited by
LEONARD I. KATZIN

Argonne National Laboratory

Part 1

Oak Ridge, Tennessee
United States Atomic Energy Commission
Technical Information Service Extension
1952

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PREFACE

With the finding by G. T. Seaborg, J. W. Gofman, and R. W. Stoughton in 1942 (Paper 1.1, this report) that the isotope U^{233} undergoes fission with slow neutrons with a cross section comparable to that of U^{235} , a third source of nuclear energy was added to the already known U^{235} and Pu^{239} . The development of the chain-reacting pile by the physics group at Chicago in 1942 opened the way for the large-scale conversion of relatively abundant natural thorium into U^{233} . The study of the properties of U^{233} and processes for obtaining it was therefore made part of the program of the Manhattan Engineering District, or Manhattan Project.

This report contains the assembled record of the significant work relating to U^{233} which was done on the Manhattan Project, from the discovery by Seaborg, Gofman, and Stoughton to July 1, 1945, when, following V-E Day and the assured success of the wartime aims of the venture, the technical staff of the Manhattan Project was slashed. This is the experimental work which in normal peacetime circumstances would have appeared as individual papers in the appropriate scientific journals. A few papers, principally among those relating to nuclear transformations and nuclear properties, embody experimental work extending one or two years later than the date given. The largest volume of the material covers data obtained before July 1, 1945, and was assembled from unpublished data and data which had appeared in scattered progress reports and memoranda of the Manhattan Project by the experimenters themselves. The only editorial alterations of these manuscripts have been those requested by the publisher's technical editorial staff at Oak Ridge, and these have been largely changes to follow their style pattern, to rectify mechanical errors of typography in the manuscripts submitted, and to repair accidental omissions. Since the original authors were for the most part unavailable, the editor has acted to supply omitted material, to determine the author's intent in cases of discrepancies or ambiguities, and to protect the authors against alteration of the scientific meaning and intent of the original manuscripts in the process of technical editing. It is hoped that failures in this respect are a minimum.

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PRODUCTION AND SEPARATION OF U²³³

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LEONARD I. KATZIN

Argonne National Laboratory

Part 2

Oak Ridge, Tennessee
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Paper 1.1

A NEW FISSIONABLE ISOTOPE OF URANIUM: U^{233}

By Glenn T. Seaborg, John W. Gofman, and Raymond W. Stoughton

[Editor's Note: Contribution from the University of California Radiation Laboratory, Berkeley; based on Report CN-126 (A-192). Prepared for publication June 11, 1942.]

1. INTRODUCTION

The bombardment of thorium with slow neutrons produces Th^{233} by the reaction $Th^{232}(n,\gamma)Th^{233}$, which emits beta particles and has a half life of 23.5 min. The daughter of Th^{233} is the 27.4-day beta-emitting^{1,2} Pa^{233} , which in turn decays to U^{233} . This decay chain can be summarized as follows:

We have measured the radioactivity and fission properties of U^{233} . This isotope has a half life of about 1.2×10^5 years and emits alpha particles having a range of 3.1 ± 0.2 cm. Our measurements on a sample of U^{233} weighing 3.8 μg show that this isotope undergoes fission with slow neutrons with a cross section about 1.3 times as great as that of U^{235} . The same result was obtained in a check experiment with another sample of U^{233} weighing 0.8 μg . We have made a search for spontaneous fission in U^{233} , using the 3.8- μg sample, and our result of zero fission counts in 243 hr of counting time indicates that the spontaneous fission rate may correspond to a half life of more than 10^{14} years. These results have been reported in a short abstract.³

This paper describes all the experiments which have been performed in order to obtain these measurements. Section 2 describes the instrument-calibration experiments; Sec. 3 describes the measurements of the radioactivity properties of U^{233} (and also Pa^{233} and

Th²³³); Sec. 4 summarizes the fission measurements on U²³³, Sec. 5 outlines the chemical procedures used in this work; and Sec. 6 discusses the yield in the production of radioactive U²³³.

The samples were prepared by the bombardment of thorium nitrate with the neutrons formed in the 60-in. Berkeley cyclotron when beryllium was bombarded with deuterons. The 3.8- μ g sample of U²³³, upon which the fission measurements as described in Sec. 4 were made, and the smaller sample, upon which the half-life measurements as described in Sec. 3 were made, were both prepared as the result of the bombardment of about 5 kg of thorium nitrate. They were put in saturated aqueous solution which was placed directly behind the beryllium target and bombarded during the course of several weeks with about 14,000 μ a-hr of deuterons on beryllium.

Each of these samples was isolated by the chemical procedures described in Sec. 5. The calibration experiments of Sec. 2 were performed both with Pa²³³ obtained from this bombardment and with Th²³³ and Pa²³³ obtained in shorter bombardments of small amounts of thorium nitrate.

2. CALIBRATION EXPERIMENTS

The beta particles were counted (1) with Geiger-Mueller counter tubes, (2) with Lauritsen electroscopes, and (3) with an ionization chamber connected to an FP-54 electrometer tube, depending upon the intensity of the samples. It was necessary to calibrate these instruments in an absolute manner for the radiations of the various radioactive isotopes involved in this research. The alpha-emitting samples were mounted for counting by placing them on metal disks. These disks were designed so that they could serve as one electrode of an alpha-counting ionization chamber. This alpha-counting ionization chamber was calibrated by depositing electrolytically a weighed amount of uranium on a disk, which served as one electrode of the ionization chamber, and then determining the alpha-counting rate of this weighed sample. In this manner we determined that this, our "inside chamber," had a counting efficiency of 45 per cent. For the measurement of alpha activities of higher intensity the samples were placed outside an alpha-counting ionization chamber which had a screen window, and for very high intensities the efficiency was further cut down by interposing additional screens between the sample and the ionization chamber. One alpha-counting ionization chamber was equipped with a magnet for bending out beta particles. The ionization chambers were connected to linear pulse amplifiers; scale-of-one or scale-of-eight recording systems were used, depending upon the experiment.

The Geiger-Mueller counter was of the bell jar type, about 5 cm long and 3 cm in diameter with a thin-mica window 3 mg/cm² thick. The central wire of the tube extended to within a few millimeters of this thin-mica window and had a glass bead on its end. The beta-emitting samples, mounted in the various experiments on copper, platinum, cardboard, cellophane, etc., were placed in a standard position within a few millimeters of this mica window. The geometrical efficiency of this counting arrangement was determined by counting the UX₂ beta particles from a weighed amount of uranium. In addition to this, a sample of RaD, in equilibrium with RaE and Po, was used in the calibration for efficiency; the Po alpha particles were counted with the calibrated alpha-counting ionization chamber, and the corresponding RaE beta particles were counted in the standard position with the Geiger-Mueller counter. A similar experiment was performed using AcB and its decay products. The samples were all mounted on cellophane in order to eliminate the effect of back-scattering. The average of all these determinations gave 29 ± 2 per cent as the geometrical efficiency of the Geiger-Mueller counting arrangement.

It was necessary to determine the absolute efficiency of the Lauritsen electroscope and the FP-54 ionization chamber for the measurement of the intensity of the Pa²³³ radiation because the absolute number of millicuries of Pa²³³ had to be known in order to be able to determine the half life of U²³³. These calibrations were accomplished by counting aliquot samples of Pa²³³ mounted on cellophane with the Geiger-Mueller counter, the Lauritsen electroscope, and the FP-54 ionization chamber. The Lauritsen electroscope had an aluminum window of thickness about 3 mg/cm², and the FP-54 ionization chamber had an aluminum window of thickness about 0.1 mg/cm².

Since a number of important Pa²³³ samples were mounted on copper disks it was necessary to determine the amount of back-scattering of Pa²³³ particles which occurred from the copper. This was accomplished by measuring two Pa²³³ samples of identical strength, one mounted on cellophane and the other on a copper disk. With the FP-54 ionization chamber the sample mounted on copper gave a reading which was 49 per cent greater than that of the sample mounted on cellophane, and this back-scattering correction was applied when it was necessary to determine the absolute amount of Pa²³³ radiation in a sample mounted on copper.

Another very important factor which had to be taken into account was the fact that the Pa²³³ radiation contains a large number of conversion electrons in addition to the beta particles in the Geiger-Mueller counter calibration experiment. However, it is the absolute intensity of the

Pa^{233} beta particles from which the half life of U^{233} must be calculated. The number of conversion electrons per beta particle from Pa^{233} was determined by preparing a strong, chemically purified sample of 23.5-min Th^{233} and allowing it to decay to the 27.4-day Pa^{233} , counting the particles from the Th^{233} and the Pa^{233} with the Geiger-Mueller counter. In this manner, assuming that there are no conversion electrons present in the Th^{233} radiation, it was determined that there are about 1.3 conversion electrons per beta particle in the Pa^{233} radiation. (This includes conversion electrons with energies down to the order of tens of thousands of electron volts; and, in order to obtain this figure, the correction for the absorption of the particles in the Geiger-Mueller counter window was determined by measuring the absorption of the particles, using for this the thin-window FP-54 ionization chamber.)

Thus it can be seen that the 27.4-day Pa^{233} , because of its conveniently long half life, was used as an intermediary in the determination of the half life of U^{233} ; actually, therefore, it is the ratio of the number of Th^{233} particles (assuming no conversion electrons in the Th^{233}) to the corresponding number of U^{233} alpha particles that was used in the determination of the half life of U^{233} in these experiments. Of course the weight of U^{233} in our samples is calculated with the use of the U^{233} half life, so that this measurement enters into our fission cross-section determination.

3. MEASUREMENT OF RADIOACTIVITY PROPERTIES

In order to determine the half life of U^{233} a strong sample of Pa^{233} was isolated chemically from the strongly neutron-irradiated sample of thorium nitrate. The chemical procedure, which was designed to eliminate even microgram amounts of uranium and thorium impurity from the final sample, is described in Sec. 5. The final sample was isolated electrolytically on a copper disk and had a thickness of carrier material of less than 0.2 mg/cm^2 . The measurement of this sample on the calibrated FP-54 ionization chamber showed, after correction for the back-scattering of the particles from the copper and correction for the conversion electrons, that there were 16.0 millicuries of Pa^{233} beta particles present in the sample.

This sample was then placed near an alpha-counting ionization chamber which had a screen window and which was connected to a linear pulse amplifier and scale-of-eight recording system. There was a magnetic field between the sample and the alpha-counting ionization chamber in order to bend out the major portion of the strong beta radiation without affecting the alpha particles. The geometrical counting efficiency of this arrangement was determined at a later time by count-

ing a sample of U^{233} both in this position and in the inside chamber, whose efficiency had previously been determined as 45 per cent.

An alpha activity was found to grow in this sample with the expected 27.4-day half life. It was found that the sample of 16 millicuries of Pa^{233} , after decaying to U^{233} , had a corresponding activity (at infinite time) of 375 alpha particles per second. From these two figures, 16 millicuries of Pa^{233} and 375 U^{233} alpha particles per second, it is calculated that the half life of U^{233} is 1.2×10^5 years. [An interesting observation is worth mentioning here: The 30,000-year Pa^{231} was also formed during the bombardment as a result of reactions $Th^{232}(n,2n)Th^{231}$ and $Th^{231}(UY) \xrightarrow{25h} Pa^{231}$. Consequently in the alpha-growth experiments account had to be taken of the Pa^{231} alpha particles, which were present from the beginning. The yield of Pa^{231} , correcting for half lives, amounted to about 10 per cent of the yield of U^{233} in our experiments.]

The range of the alpha particles from U^{233} was determined by measuring their absorption in thin aluminum foils and comparing this absorption with that obtained for Po alpha particles measured under the same conditions. These measurements showed that the range is 3.1 ± 0.2 cm of air ($15^\circ C$, 760 mm Hg). These data for U^{233} are the first obtained for an alpha emitter of the missing $(4n+1)$ radioactive series. It is interesting to note that this point falls near the Geiger-Nuttall curve for the uranium $(4n+2)$ series.

The data which we have obtained on the absorption and the energy of the particles from Th^{233} and Pa^{233} should be added here. The absorption in aluminum, obtained with a Lauritsen electroscope, of the 23.5-min Th^{233} beta particles showed an end point at approximately 700 mg/cm², corresponding to an upper energy limit of about 1.6 Mev (Fig. 1). The ratio of the ionization due to the beta particles to that due to the gamma rays was approximately 1000 in this absorption experiment. This ratio is normally about 100, when there is one gamma ray per beta particle, and therefore it appears that there are no nuclear gamma rays in the Th^{233} radiation; the small amount of apparent gamma rays is probably to be attributed to bremsstrahlung. The absence of gamma rays here might lend weight to the assumption that there are no conversion electrons present in the radiation of Th^{233} . The shape of the absorption curve also indicates the absence of conversion electrons.

The absorption in aluminum of the Pa^{233} radiation, obtained both with a Lauritsen electroscope and with an FP-54 ionization chamber, shows an end point at about 165 mg/cm², corresponding to an energy of about 0.5 Mev (Fig. 2). In this case the absorption curve gives evidence for the conversion electrons known to be present; the half

thickness amounts to about 5 mg/cm^2 of aluminum at the beginning of the curve, and then changes, at about 8 mg thickness, to a half thickness of about 11 mg/cm^2 (Fig. 3). The high ionizing efficiency of these low-energy particles and the high conversion coefficients of the gamma rays combine to make the ratio of beta-particle to gamma-ray ionization about 700 on the FP-54 ionization chamber. This is about what should be expected when proper account is taken of these factors. As was mentioned in Sec. 2 there are present in the Pa^{233} radiation about 1.3 conversion electrons, counting those with energies exceeding some tens of thousands of electron volts, per beta particle.

4. FISSION MEASUREMENTS

The sample upon which the main fission measurements were performed was originally isolated in the form of Pa^{233} by the chemical methods described in Sec. 5 and had a beta-disintegration rate, as measured on the FP-54 ionization chamber, of the order of 100 millicuries. After the lapse of about two months, so that about 80 per cent of the Pa^{233} had decayed to U^{233} , the U^{233} was chemically separated, by the methods described in Sec. 5, from the undecayed Pa^{233} . This was necessary since it was found to be impossible to make measurements on a sample which contained the very large amount of beta activity (about 20 millicuries) which was present when the Pa^{233} was in the sample. From the alpha activity of this final sample, together with the half life of U^{233} (1.2×10^5 years), it was calculated that the weight of the sample amounted to about $3.8 \mu\text{g}$.

This sample of U^{233} , which was on a platinum-coated copper disk and present with less than 0.2 mg/cm^2 of carrier material, was placed on one electrode of a shallow ionization chamber connected to a linear pulse amplifier which was adjusted so as to record the pulses due to fissions. The measurements were made with a 300-mg Ra-Be neutron source. The neutron source and the ionization chamber were completely surrounded with paraffin. Under these conditions 453 fission counts were obtained in 8.2 hr of counting time, corresponding to 55.2 c/hr. When the ionization chamber was surrounded with a cadmium shield 0.35 g/cm^2 thick, 161 fission counts were obtained in 17.6 hr of counting time, corresponding to 9.1 c/hr. Therefore the U^{233} fission-counting rate due to slow cadmium-absorbable neutrons amounted to about 46.1 c/hr.

The $3.8\text{-}\mu\text{g}$ U^{233} sample was then replaced by a standard $200\text{-}\mu\text{g}$ uranium sample. With this standard uranium sample, containing $1.4 \mu\text{g}$ of U^{235} , 331 fission counts were obtained in 15.5 hr of counting time, amounting to 21.4 c/hr, under the same conditions as above.

When the ionization chamber was surrounded with the cadmium shield 168 fission counts were obtained in 20.7 hr of counting time, which amounts to 8.1 c/hr. The fission-counting rate of the U^{235} due to slow neutrons was therefore 13.3 c/hr. These values, 46.1 c/hr for the 3.8- μ g U^{233} sample and 13.3 c/hr for the 1.4- μ g U^{235} sample, lead to the result that the slow-neutron fission cross section of U^{233} is about 1.3 times as large as that of U^{235} . These counting data represent the total of all the counting which was performed on the samples; in the actual experiments the various samples were alternated at frequent intervals, and a consideration of the data obtained in these shorter counting intervals shows that the measurements are statistically consistent with each other.

It should be pointed out that all the counts which were obtained when the cadmium shield was present cannot be attributed to fast neutrons; therefore a fast-neutron fission cross section for U^{233} cannot be deduced from these experiments. The cadmium shield, mostly for the reason of convenience of manipulation, was such that a small percentage of the slow neutrons might leak through to the sample. The problem of the design of apparatus for fast-neutron measurements, so as to exclude essentially all the slow neutrons, is a rather difficult one because of the relatively small fast-neutron fission cross sections. The fast-neutron fission cross-section measurements for U^{233} that were made with such apparatus are described in Paper 1.5 of this volume. Of course the fact that a small percentage of the slow neutrons is effective when the cadmium shield is present does not introduce any error into the calculation of the slow-neutron fission cross section of U^{233} because the same fraction of the slow neutrons reaches both the U^{233} and the standard U^{235} sample.

A check on this slow-neutron cross section was obtained by measuring the slow-neutron fission rate of another sample of U^{233} . This sample, which was used for the half-life determination described in Sec. 3, had a weight of 0.8 μ g of U^{233} at the time of the experiment. With this sample there were obtained 11.2 c/hr (21.8 hr of counting time) without the cadmium shield and 1.9 c/hr (11.5 hr of counting time) with the cadmium shield. This result of 9.3 slow-neutron fission counts per hour for the 0.8- μ g sample of U^{235} also leads to the result that the slow-neutron fission cross section of U^{233} is about 1.3 times that of U^{235} .

A search for spontaneous fission in U^{233} was made using the 3.8- μ g sample. This sample was placed on one electrode of an ionization chamber connected to a linear pulse amplifier and recording system whose gain was adjusted so as to count the pulses due to fissions. With this arrangement zero fission counts were observed during 243 hr of

operation. The apparatus was tested periodically during this interval by demonstrating that the fissions induced in this sample by a neutron source were being recorded with the proper efficiency. It was shown, by considering the geometry of the ionization chamber and by measuring the variation with amplifier gain of the neutron-induced fission-counting rate, that the over-all efficiency of the apparatus for recording fission amounted to about 72 per cent. Hence, for a 3.8- μ g sample the time between fission counts should be, on the average, about 180 hr for a spontaneous fission rate corresponding to a half life of 10^{14} years. Since zero counts were observed in 243 hr, it seems probable that the half life for the spontaneous fission of U^{233} is of the order of, or greater than, 10^{14} years.

5. CHEMICAL PROCEDURES

The chemical procedures for isolating Pa^{233} and U^{233} described in this section were developed by working with a number of small samples of these radioactivities formed in small bombardments and with part of the large amount of these isotopes which was obtained from the 5 kg of thorium nitrate $[Th(NO_3)_4 \cdot 4H_2O]$ that was bombarded with about 14,000 μ a-hr of deuterons on beryllium. The procedures which were used to extract the Pa^{233} and U^{233} from the 5 kg of bombarded thorium nitrate will be described in detail.

The U^{233} , after the decay of the Pa^{233} , could not be isolated directly from the bombarded thorium nitrate because it was necessary that it be absolutely free from the natural isotopes of uranium (down to less than microgram amounts), and 5 kg of thorium nitrate would certainly contain at least milligram amounts of uranium. In the preparation of the U^{233} samples, therefore, Pa^{233} was isolated first and carefully purified from uranium.

The bombarded solution of 5 kg of thorium nitrate was diluted up to 26 liters with water and then made approximately 0.5N in nitric acid. To this total solution about 400 g of manganous chloride was added. This was precipitated out from the hot solution in three separate portions by the addition of potassium permanganate to the solution. Each precipitate of manganese dioxide was centrifuged out separately. The protactinium is carried down with the manganese dioxide, more or less quantitatively, under these conditions. However, the efficiency of this protactinium precipitation seems to vary under slight changes of conditions, and it is well to have present some instrument for detecting the Pa^{233} radiation so as to follow the course of this isotope throughout the whole chemical separation. (In the case of our 5 kg of thorium nitrate, several manganese dioxide precipitations were made from it by

an identical procedure, before the neutron irradiation, in order to remove the 30,000-year alpha-emitting Pa^{231} which was found to be originally present.)

The combined manganese dioxide precipitates were dissolved in a mixture of hydrogen peroxide and hydrochloric acid. After decomposing the hydrogen peroxide by boiling, about 200 mg of zirconium oxychloride was added to this solution, the zirconium was precipitated as zirconium phosphate by the addition of phosphoric acid, and the precipitate was centrifuged out. Several further precipitations of zirconium phosphate were performed by adding further 100-mg portions of zirconium oxychloride, each precipitate being centrifuged out separately. Zirconium phosphate carries down the protactinium essentially quantitatively.

It was then necessary to remove the Pa^{233} from the rather large amount of zirconium with which it was present and to purify it from uranium and thorium. The zirconium and protactinium phosphates were brought into solution by treatment with dilute hydrofluoric acid. This step also gave a separation from thorium, which was precipitated as the insoluble fluoride at this point. This solution was cooled with ice water, and zirconium and protactinium hydroxides were precipitated by adding dilute sodium hydroxide solution; the solution must be kept cold in this precipitation or difficulty will be experienced in redissolving the precipitated hydroxides. The hydroxide precipitate was then dissolved in nitric acid, and the protactinium was carried away from most of the zirconium by another series of manganese dioxide precipitations. Some of the zirconium came along with the manganese dioxide precipitate in this procedure, so that a further removal of the zirconium, as well as the manganese, from the protactinium was necessary. This involved going through the above-described cycle two more times, finally ending up with a small zirconium phosphate precipitate containing the protactinium.

This zirconium phosphate precipitate, which now contained only about 10 mg of zirconium, was dissolved in hydrofluoric acid and, after precipitation of the hydroxide as described above, was converted to the nitrate by dissolving the hydroxide in nitric acid. Another precipitation of the zirconium phosphate was then made in order to be sure that all the uranium and thorium in amounts less than a microgram were removed. The final zirconium phosphate was converted into zirconium sulfate by means of the method of dissolving in hydrofluoric acid, precipitating the hydroxide, dissolving the hydroxide in sulfuric acid, and evaporating to dryness.

The final zirconium sulfate (containing about 10 mg of zirconium) was dissolved in about 30 cc of 0.33M ammonium fluoride solution,

and the hydrogen-ion concentration of the solution was adjusted until it corresponded to that of the methyl red indicator end point. The Pa^{233} was then isolated by an electrolytic procedure; in this procedure the Pa^{233} is deposited in a very thin adherent layer and is separated from the zirconium at the same time. In our experiment the electrolysis chamber consisted of a clear bakelite chamber fitted with a brass plug which screwed into the lower end. On this plug rested the copper disk on which the Pa^{233} was deposited. This copper disk served as the cathode, and a motor-driven platinum stirrer served as the anode. The electroplating was carried out for about 8 hr at about 100 ma current, with about 15 volts across the tube (the actual electrode potential is not known). The Pa^{233} is plated out nearly quantitatively (about 90 per cent) under these conditions, and the plate usually appears as a dark-brown or black well-adhering film, probably platinum, of entirely negligible weight (about 0.2 mg/cm^2). No zirconium plates out under these conditions, so that a good separation of protactinium from zirconium is obtained by this procedure. Two samples were prepared by this procedure. One had a beta-disintegration intensity of about 16 millicuries and was used for the half-life determination described in Sec. 3. The other sample had a beta intensity of the order of 100 millicuries and was prepared for use in the fission measurements described in Sec. 4.

After the 100-millicurie sample had decayed for about two months the U^{233} was separated from the undecayed Pa^{233} . In order to do so it was necessary to separate some $4 \mu\text{g}$ of U^{233} from about $1 \mu\text{g}$ of undecayed Pa^{233} . This procedure was carefully worked out using U^{233} and Pa^{233} activities as tracer isotopes, and the procedure is described in the following paragraphs. The final sample of U^{233} was again deposited by an electrolytic procedure.

The thin film containing the Pa^{233} and U^{233} , and probably some platinum, was dissolved in 6N hydrochloric acid to which a few drops of 6N nitric acid had been added. Since a small amount of copper was dissolved from the backing plate in this procedure, this was removed by a H_2S precipitation from the acid solution. No Pa^{233} or U^{233} was carried down by the copper sulfide in this precipitation. After the removal of the H_2S and the reduction of the amount of 6N hydrochloric acid to about 2 cc by boiling the solution, about 0.1 mg of zirconium as zirconium oxychloride was added. There was then added a few thousandths of a cubic centimeter of 85 per cent phosphoric acid, and the precipitated zirconium phosphate was removed by centrifugation.

The major portion of the Pa^{233} , perhaps 70 per cent or more, was removed in this step. The yield of Pa^{233} in this precipitate is lower than that obtained when a large excess of phosphoric acid is used;

however, an excess of phosphoric acid must be avoided because the acidity of the solution must be kept very low in the electrolytic procedure which follows. It was essential that less than 0.1 per cent of the Pa^{233} remain with the U^{233} , and hence further separations were necessary. These further separations of the Pa^{233} from the U^{233} were effected by adding zirconium, about 0.1 mg at a time, in successive portions to the solution. The Pa^{233} was not carried down so quantitatively by the zirconium phosphate under these conditions; therefore it was necessary to make about 15 precipitations of zirconium phosphate by the addition of zirconium to the phosphoric acid solution in this manner. However, after performing this number of precipitations, less than 0.1 per cent of the Pa^{233} remained in the solution. Practically all the U^{233} remains in solution in this procedure, but it should be emphasized that in order for this to be the case it is necessary that the Pa^{233} be removed with small portions of zirconium phosphate in the manner which has been described.

The volume of the solution was then reduced, by evaporation, to a volume of about 0.1 cc. To this solution, which contained about 0.10 cc of 6N hydrochloric acid and of the order of 0.001 cc of 85 per cent phosphoric acid, there was added 0.02 cc of glacial acetic acid, and the solution was diluted by the addition of 5 cc of water. This solution was placed in the electrolysis chamber, which consisted of a clear bakelite chamber fitted with a brass plug which screwed into the lower end and upon which rested the platinum foil that the U^{233} was to be deposited on. The electroplating was carried out for about 8 hr at about 90 ma current, with about 8 volts across the tube (the actual electrode potential is not known). The U^{233} is plated out nearly quantitatively (greater than 90 per cent) under these conditions, and the plate usually appears as a dark-brown or black well-adhering film, probably platinum, of entirely negligible weight (about 0.2 mg/cm^2). It should be emphasized that in order for the uranium to be quantitatively deposited the acidity of the solution must be kept very low, as described above. (In addition, it may be pointed out that this electrolysis may be performed from a 0.3M ammonium fluoride solution, with approximately the same yield, and in some experiments we have used this procedure.) The weight of the large U^{233} sample prepared in the manner outlined above was determined from its alpha activity and from the half life of U^{233} (1.2×10^5 years). As previously mentioned, this weight amounted to $3.8 \mu\text{g}$.

Since zirconium is often used as a carrier for small amounts of protactinium, it seems advisable to say a word about the methods which we have developed for separating protactinium from zirconium. The best method is the electrolysis from ammonium fluoride solution, described above, wherein microgram (or less) quantities of protactinium

are deposited while as much as 10 mg of zirconium remains in solution. Another method is the precipitation of the protactinium with manganese dioxide, previously described. In this procedure a certain amount of zirconium is also carried along with the manganese dioxide; this small amount of zirconium can be removed from the manganese by precipitation as zirconium phosphate which carries the protactinium with it. After dissolving the zirconium-protactinium phosphate in HF, etc., the protactinium can be removed by another manganese dioxide precipitation, and this cycle may be repeated as often as is necessary in order to remove practically all the zirconium from the protactinium. In a third method the protactinium is removed with lanthanum oxalate by making a number of successive precipitations of lanthanum oxalate from a dilute hydrochloric acid solution; six or eight precipitations will carry about 80 per cent of the protactinium while carrying a negligible amount of the zirconium, which remains in solution as a complex oxalate. (The protactinium can then be removed from the lanthanum oxalate by dissolving the latter in hydrochloric acid and precipitating a very small amount of zirconium phosphate from this solution.) A fourth method involves the fractional precipitation of zirconium iodate. If there is added to a 1N to 6N HCl or HNO_3 solution, containing a mixture of zirconium and protactinium, a small amount of sodium iodate sufficient to precipitate only a small fraction of the zirconium as zirconium iodate, it is found that the protactinium concentrates to a large extent in this first fraction. This precipitate can be dissolved in concentrated hydrochloric acid, and again a partial precipitation of zirconium iodate can be performed; in each cycle a large concentration of protactinium is obtained. By removing several zirconium iodate precipitates in each cycle, the protactinium can be brought along quantitatively. Finally there is the fractional crystallization⁴ of zirconium oxychloride from 6N to 10N HCl solution, in which the protactinium concentrates in the mother liquor.

6. YIELDS

It seems worth while to append the rough yield data obtained from a consideration of the results of the bombardment of 5 kg of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ with the neutrons from 14,000 $\mu\text{a-hr}$ of deuterons on beryllium. The total yield from all the fractions in this bombardment amounted to about 7 or 8 μg of U^{233} , amounting to about 1 μg per 2000 $\mu\text{a-hr}$. One microgram of 120,000-year U^{233} corresponds to the order of 0.01 microcurie of alpha activity. The isotope U^{233} is useful as a tracer for microgram, and less than microgram, amounts of uranium, and a large number of tracer experiments can be performed with a few hundredths

of a microcurie of alpha activity. It is expected that larger yields can be obtained by bombarding larger amounts of thorium, perhaps in the form of the oxide rather than the nitrate and perhaps by maintaining a lower ratio of hydrogen to thorium nuclei by performing the bombardment on solid hydrated materials rather than on saturated solutions.

Fig. 1—Absorption in aluminum of 23.5-min Th^{233} radiation (Lauritsen electroscope).

Fig. 2—Absorption in aluminum of 27.4-day Pa^{233} radiation (Lauritsen electroscope).

Fig. 3—Absorption of 27.4-day Pa^{233} radiation in thin aluminum foil (FP-54 ionization chamber).

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Paper 1.2

DETERMINATION OF THE HALF LIFE OF U^{233}

By Earl K. Hyde

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ABSTRACT

The half life of the alpha-emitting isotope U^{233} has been redetermined to be $1.62 \pm 0.01 \times 10^5$ years.

1. INTRODUCTION

The half life of the alpha-emitting radioactive isotope U^{233} was originally determined by Seaborg, Gofman, and Stoughton¹ to be 1.2×10^5 years. The amounts of U^{233} available to them were so minute that an indirect method had to be employed. This method consisted in measuring the rate at which alpha particles were emitted following the complete decay of a strong sample of Pa^{233} (which had been isolated chemically from a strongly neutron-irradiated sample of thorium nitrate). The nuclear transformations involved may be represented as

From the total alpha activity resulting from the complete decay of 16 millicuries of Pa^{233} activity, the half life of U^{233} was calculated.

In this method the experimentally measured activities were subject to a number of large corrections as a result of the following factors:

1. The observed Geiger-Mueller activity included a high percentage of conversion electrons (1.3 conversion electrons per Pa^{233} beta particle).

2. The back-scattering of the Pa^{233} beta particles from the copper disks on which the samples were mounted was high (49 per cent).

3. Ten per cent of the observed alpha activity represented Pa^{231} activity resulting from an (n,2n) reaction in the original bombardment.

4. The counting-yield factor of the alpha counter used was 45 per cent. Since the presently accepted figure for the counting yield of the same type of alpha counter is 52 per cent,² this may have introduced an error of several per cent.

Uncertainties in the corrections necessitated by these factors reduced the accuracy of the determination and made it desirable to repeat the determination by a direct method when more material was available. This has now been done with samples of several milligrams of chemically pure U^{233} . The new value obtained for the half life is $1.62 \pm 0.01 \times 10^5$ years.

2. PREPARATION AND PURIFICATION OF U^{233}

The uranium used in the determination was produced by irradiation of thorium for several months with the neutrons of the uranium-graphite chain-reacting pile at Oak Ridge National Laboratory. An ether extraction of the solution formed by the dissolution of the irradiated thorium in nitric acid was employed to extract the uranium from the large quantities of thorium and from smaller amounts of protactinium, fission products, and other impurities. One sample of U^{233} was isolated in this way by Hagemann, Katzin, and Studier;³ a second sample was later isolated from a separate batch of irradiated thorium by Hagemann.⁴

For further assurance of chemical and radiochemical purity these samples were subjected to several precipitations including those of ammonium diuranate by ammonia, sodium uranyl acetate from dilute acetic acid solution, and uranyl peroxide by 10 per cent hydrogen peroxide. The final treatment was an ether extraction from a solution 0.2N in nitric acid and saturated with ammonium nitrate.

3. DETERMINATION OF ISOTOPIC PURITY

It was necessary to measure the specific alpha disintegration rate and the isotopic purity of the uranium samples in order to calculate the half life of pure U^{233} . The isotopic purity was determined, through the kind cooperation of A. J. Dempster and members of his section, by mass-spectrographic analysis.⁵

Using uranium tetrafluoride samples prepared by Hagemann³ and employing a direct electrometer comparison of the ions collected, including a correction for the scattering of the U^{233} atoms to the U^{238}

position, these investigators found the U^{233} content to be 96.4 ± 0.4 per cent in these samples.⁵ It is fortuitous that these two U^{233} preparations had identical isotopic purities.

The source of the U^{238} isotope found as an impurity was a small concentration of natural uranium in the thorium used in the production of the U^{233} .

4. DETERMINATION OF THE SPECIFIC ACTIVITY

A sample of the purified U^{233} was ignited to U_3O_8 in a weighed platinum crucible at $750^\circ C$. This oxide was dissolved in nitric acid, quantitatively transferred to a calibrated volumetric flask, and diluted to volume. Aliquots ranging in size from 50 to 250 μl were removed by means of calibrated micropipets, transferred to separate volumetric flasks, and diluted to volume. Aliquot samples of the resulting solutions were mounted on platinum disks and counted in a standard pulse ionization chamber.² A resolution loss correction of 0.8 per cent per 1000 c/min was applied. In one case, instead of making a dilution, aliquot samples of the first solution were mounted on counting disks and counted in a nitrogen-filled alpha counter equipped with a scale-of-64 scaling circuit.² With this counter the coincidence correction was negligible. The samples were counted for a length of time sufficient to reduce the probable fractional error to less than 0.3 per cent.

The contribution of the U^{238} impurity to the measured alpha activity is entirely negligible, since it is approximately a one-millionth part of the total activity.

5. RESULTS

Summarized in Table 1 are the details of the individual determinations.

The best value of the half life is $1.62 \pm 0.01 \times 10^5$ years. Possible error in the 52 per cent counting-yield factor² used in the calculations is not included in the limits of error. When this factor is determined directly for samples mounted on platinum and emitting particles of the energy of the U^{233} alpha particle, a recalculation of the half-life value may be necessary.

6. ACKNOWLEDGMENTS

The author wishes to thank L. I. Katzin for suggesting the problem and for many helpful suggestions. The assistance of M. H. Studier in carrying out one of the specific-activity determinations is gratefully acknowledged.

Table 1

Determination *	1	2	3
Weight oxide, mg	5.273	8.15	1.49
Mass-spectrographic analysis ⁵			
U ²³³ , %	96.4 ± 0.4	96.35 ± 0.4	96.35 ± 0.4
U ²³⁸ , %	3.6 ± 0.4	3.65 ± 0.4	3.65 ± 0.4
Volume of first solution, ml	25.0	50.0	10.00
Number of dilutions	4	1	0
Number of aliquots counted	10	2	2
Mean corrected aliquot count	1895	723	13,200
Dilution factor†	2.49 × 10 ⁴	1.000 × 10 ⁵	1.000 × 10 ³
Counting yield, %	52	52	52
Calculated specific activity, dis/min / μg of pure U ²³³	2.11 × 10 ⁴	2.09 × 10 ⁴	2.09 × 10 ⁴
Calculated half life, years	1.61 × 10 ⁵	1.63 × 10 ⁵	1.63 × 10 ⁵

*The U²³³ isolated by Hagemann, Katzin, and Studier³ was used in determination 1. The U²³³ used in determinations 2 and 3 was isolated in a later preparation by Hagemann.⁴

†The dilution factor is the number by which the aliquot count must be multiplied to give the alpha count of the entire sample.

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Paper 1.3

RADIATION SPECTRUM OF THE TRANSITION $U^{233} \rightarrow Th^{229}$

By Martin H. Studier

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ABSTRACT

A complex radiation spectrum consisting of 310-, 80-, and 40-Kev gamma rays, L x-rays, and conversion electrons is shown to be associated with the transition $U^{233} \rightarrow Th^{229}$. The 80- and the 40-Kev gamma rays seem to be largely converted.

1. INTRODUCTION

When weighable quantities of U^{233} , the 1.6×10^{-5} year alpha emitter,¹ first became available, it was observed that a considerable amount of Geiger-Mueller activity was associated with the uranium. To determine the nature of these radiations a series of absorption curves with lead, copper, aluminum, and beryllium was run. These curves indicated a complex radiation spectrum consisting of gamma rays, x-rays, and conversion electrons. The various components in the absorption curves were resolved by successively subtracting the harder components from the original curves. Although the determination of the characteristics of the components of a complex radiation by this method is only an approximation, measurements with a beta-ray spectrograph, which require thin samples, are not feasible because of the low specific activity of U^{233} and the low abundance of gamma rays.

Presumably the gamma rays originate from excited nuclei of Th^{229} formed by the transition $U^{233} \rightarrow Th^{229}$, while the electrons and x-rays arise from internal conversion of gamma rays.

2. EXPERIMENTAL WORK

The U^{233} used in these experiments was purified by ether extractions and a series of precipitations as sodium uranyl acetate, ammonium diuranate, and uranyl peroxide. Throughout the chemical purification the Geiger-Mueller activity remained in a constant ratio to the alpha activity, and it was therefore assumed to be associated with radioactively pure U^{233} .

Cylindrical brass-walled argon-filled Geiger-Mueller tubes with very thin mica windows (3 mg/cm^2) were used for the absorption measurements.² The tubes were mounted in a fixed position with a set of aluminum shelves in which samples and absorbers could be placed. Absorbers were always placed as near the window as possible.

Although the available supply of U^{233} was adequate for the measurements on the L x-rays and conversion electrons, it was hardly sufficient for an accurate study of the harder components of the radiation. Early measurements were made with a Geiger-Mueller tube which was completely surrounded with paraffin to minimize scatter of radiation. However, it was found that appreciable scattering of electromagnetic radiation from either the paraffin or the aluminum shelves occurred and resulted in fictitious hard components in the absorption curves. This difficulty was eliminated by wrapping the tube with $\frac{1}{2}$ in. of lead.

The final measurements on the harder components of the radiation were made with U^{233} as fused uranyl nitrate spread evenly over the bottom of a 2-cm Nessler tube. The Nessler tube was placed in an upright position above the window of an inverted Geiger-Mueller tube. The bottom of the Nessler tube was equivalent to 0.375 g of aluminum absorber. Absorption curves for lead, copper, and aluminum were taken by placing the absorbers directly on the window of the Geiger-Mueller tube. Because of the low absorption coefficient in aluminum it was not possible to place enough aluminum absorbers between the sample and the counting tube to resolve the harder gamma rays. The absorption curves with lead and copper indicate the presence of a gamma ray with mass-absorption coefficients, μ/ρ , of 0.392 and $0.109 \text{ cm}^2/\text{g}$, respectively (see Fig. 1). From the data of Jones³ relating the mass-absorption coefficients in lead with energy and extrapolation of the data of Cuykendall⁴ for copper, this represents a gamma-ray energy of 310 Kev. Using the extrapolated counting yield of 150 c/min, an estimated geometry factor of 8.0 per cent, a counting efficiency of 0.5 per cent,² and the known alpha-disintegration rate of the sample, it was calculated that the gamma emission rate is 0.3 per 1000 alpha disintegrations. From the curves of Fig. 1 it can

be seen that, if any harder gamma rays are associated with the alpha disintegration of U^{233} , they must be much less abundant.

Two other components were resolved from the lead and copper absorption curves of Fig. 1 by subtraction of the harder components as shown in Figs. 2 and 3, respectively. From the lead curve the mass-absorption coefficients for the two components were estimated to be 2.42 and 14.26. The latter corresponds to an energy of 40 Kev.² The former may be either 78.5 or 138 Kev depending on which side of the K absorption edge of lead (87.8 Kev) the energy lies.² However, the copper curve indicates that the energy of this gamma ray falls below the K absorption edge of lead since a mass-absorption coefficient of 0.666 corresponding to an energy of 82 Kev was obtained.⁴ The mass-absorption coefficient of the other component with copper was estimated to be 4.28 which again corresponds to an energy of 40 Kev.⁴ There thus seem to be gamma rays of approximately 80- and 40-Kev energy associated with the decay of U^{233} . K x-rays, although probably present, were not detected because of the low emission rate of the only gamma ray with sufficient energy to be converted in the K shell (the 310-Kev gamma ray) and the low counting efficiency for a thorium K x-ray (95 Kev).

The next softer component which had the energy of L x-rays was examined on a smaller sample by absorption with aluminum. A sample of U^{233} as U_3O_8 spread evenly on platinum over an area of 1 cm² was used. The presence of negative particles, in all probability conversion electrons, was detected by bending the particles through a 180-deg angle into the window of a Geiger-Mueller tube with a magnetic field of known polarity. Absorption curves with lead, copper, and aluminum indicated the electromagnetic nature of all but the very softest radiation (conversion electrons) by the marked differences in absorption coefficients (see Fig. 4).

The aluminum absorption curve was analyzed for the various components in the radiation. A complete absorption curve, taken with the sample at a position of 10 per cent geometry and with 5.0 mg/cm² of air and window between the sample and the sensitive volume of the counting tube, is shown in Fig. 5. The hardest component indicated represents an average of the three gamma rays mentioned above. The next two components, with mass-absorption coefficients in aluminum of 5.58 and 13.86 (corresponding to energies of 17.0 and 12.5 Kev, respectively),⁵ are undoubtedly L x-rays resulting from internal conversion of gamma rays. The $L\alpha_2$, $L\alpha_1$, $L\beta_2$, $L\beta_1$, and $L\gamma_1$ lines of thorium have energies of 12.78, 12.93, 15.58, 16.16, and 18.93 Kev, respectively.⁵ The 17.0-Kev component probably represents an average of the last three lines and the 12.5-Kev component an average of the first two with perhaps some contribution from a softer radiation.

Two additional components were resolved as shown in Fig. 6. The harder of these two, with a mass-absorption coefficient of 96, seems to be at least partly electromagnetic because it appeared in absorption curves with aluminum taken with 235 mg/cm² of beryllium directly over the sample. This much beryllium should completely remove a particulate radiation with such a high absorption coefficient while reducing an electromagnetic radiation by about a factor of 2. The counting yield of this component with beryllium was about one-fourth the yield without beryllium. This indicates that the contributions of particulate and electromagnetic radiation are approximately equal. The addition of beryllium seemed to harden the component somewhat and indicated that the energy of the electromagnetic radiation is in the neighborhood of 7.0 Kev. Since this energy does not correspond to that of any x-ray of thorium, a very soft gamma ray may be present; on the other hand, it may merely be an artifact of the aluminum absorption curve. At least some of the particles which were apparently absorbed by the beryllium probably originated from conversion of the 310-Kev gamma ray and were detected, whereas K x-rays were not, because of the very much higher counting efficiency for particles. The softest component detected was shown to consist largely, if not entirely, of conversion electrons by deflecting the particles in a magnetic field. These electrons very likely result from conversion of the 80-Kev gamma ray since they are too soft to be conversion electrons from the 310-Kev gamma ray, and the electrons from conversion of the 40-Kev gamma ray would be too soft to penetrate the window of the counting tube.

3. SUMMARY AND DISCUSSION

An attempt was made to calculate the relative abundance of the various components from the extrapolated yields at zero absorber. The values are only rough approximations because of the uncertainties involved in such extrapolations and because the counting efficiency of the tubes used for electromagnetic radiation is not accurately known. The value for the yield of the 310-Kev gamma ray is fairly accurate since the counting efficiency for this energy was experimentally determined to be 0.5 per cent.² The shape of the curve, relating counting efficiency with energy for brass tubes in the energy region where counting takes place as the result of the ejection of electrons from the walls and negligible absorption occurs in the counting gas, has been determined by others.^{6,7} The experimental point at 310 Kev served as a calibration. The value of the counting efficiency for the softer components was then obtained by extrapolation of the "wall

effect'' and by calculation of the total absorption in the counting gas. The results are summarized in Table 1.

The great abundance of L x-rays (approximately one for every five alpha particles) with no detectable K x-rays is further evidence for gamma rays which are too soft to convert in the K shell but are converted in the L shell. Since the conversion electrons from the 80-Kev gamma ray are about eight times as abundant as the gamma ray itself, the gamma ray seems to be largely converted. Since the degree of conversion increases with decreasing gamma-ray energy, it is reasonable to assume that the 40-Kev gamma ray is also largely converted. This assumption is also necessary to explain the abundance of the L x-rays since the electrons from conversion of the 80-Kev gamma ray are present to the extent of only about one per hundred alpha particles and one L x-ray is present for every five alpha particles.

The fact that a complex gamma-ray spectrum is associated with the decay $U^{233} - Th^{229}$ is evidence for a complex alpha-ray spectrum. Routine analyses of U^{233} samples with a differential pulse analyzer⁸ have revealed no inhomogeneity in the alpha-ray spectrum; however, the relative emission rate of the 310-Kev gamma ray is so low and the energy difference represented by the other gamma rays is so small that the corresponding alpha spectral lines would not have been resolved. A careful analysis of the alpha-ray spectrum should reveal its complexity.

4. ACKNOWLEDGMENTS

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Table 1

Mass-absorption coefficient (μ/ρ), cm ² /g			Energy, Kev	Disintegrations per 1000 alpha disinte- grations of U ²³³	Assumed counting efficiency, %	Probable type of radiation
Pb	Cu	Al				
			<80	8.3	100	Conversion elec- trons from 80- Kev gamma ray
			200-300	1.0	100	Conversion elec- trons from 310- Kev gamma ray (?)
		87	7.0	21.0	2.8	Gamma ray (?)
		13.9	12.5	100	0.9	L α_1 and L α_2 x-rays
		5.6	17	100	0.5	L β_1 , L β_2 , and L γ_1 x-rays
14.26	4.28		40	1.7	0.3	Gamma ray
2.42	0.666		80	1.0	0.3	Gamma ray
0.392	0.109		310	0.30	0.5	Gamma ray

Fig. 1 — Analysis of lead and copper absorption curves of the gamma radiation from $U^{233} - Th^{229}$.

Fig. 2 — Analysis of lead absorption curve of the gamma rays from $U^{233} \rightarrow Th^{229}$.

Fig. 3 — Analysis of copper absorption curve of gamma rays from $U^{233} \rightarrow Th^{229}$.

Fig. 4—Lead, copper, and aluminum absorption curves of radiation from $U^{233} - Th^{229}$.

Fig. 5 — Analysis of aluminum absorption curve of radiation from $\text{U}^{233} \rightarrow \text{Th}^{229}$ showing the presence of L x-rays.

Fig. 6 — Analysis of aluminum absorption curve of very soft radiation from $U^{233} \rightarrow Th^{229}$; air + window = 5 mg/cm^2 . ---, original absorption curve before subtraction of the harder components.

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Paper 1.4

THE (4n+1) RADIOACTIVE SERIES: DECAY PRODUCTS OF U²³³

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ABSTRACT

The path of the artificially produced (4n+1) radioactive decay series between U²³³ and Bi²⁰⁹ and the properties of the individual members of the chain are shown to be as follows:

1. INTRODUCTION

The three families of radioactive heavy isotopes found in nature are differentiated by their mass characteristics. Thus the family represented by thorium (Th²³²) and its decay products has masses corresponding to the formula (4n+0); the family represented by U²³⁸ and its decay products corresponds to (4n+2); and the family represented by U²³⁵ and its decay products corresponds to (4n+3), where n in all

cases represents an integral multiplier. The family corresponding to the formula $(4n+1)$ has not been found in nature, except for the stable end member of the chain, bismuth (Bi^{209}).

Previous experiments in artificial production of nuclei have resulted in the formation of the isotopes Pb^{209} (reference 1), Th^{233} (references 2 and 3), Pa^{233} (references 3-5), U^{233} (reference 6), and Np^{237} (reference 7), whose masses correspond to the $(4n+1)$ formula. From the isotope Np^{237} (which decays by emission of an alpha particle) beta active Pa^{233} and from it alpha active U^{233} are formed by successive decays. Therefore Np^{237} may be considered to represent the long-lived parent of a $(4n+1)$ radioactive-decay family, and in analogy with natural series this may be called the neptunium series.⁸

The purpose of this paper is to trace the path of the decay chain between the isotopes U^{233} and Bi^{209} and to give the properties which have been found for the isotopes which are members of the chain. The findings may be summarized as in Fig. 1 and Table 1. Work in another laboratory, where parallel studies have been made of the U^{233} decay chain,⁹ has resulted in essentially similar findings.

Various predictions have been made in the literature with regard to the properties of the $(4n+1)$ series. Russell¹⁴ suggested the following decay scheme:

On the basis of analogy with the three known series Ra^{225} was predicted to be alpha active, decaying to alpha-active Em^{221} . Later Widdowson and Russell¹⁵ revised this prediction to suggest branching decay of Ra^{225} and beta decay of the emanation isotope. The chain would thus proceed through isotopes of elements 87 and 85 to predominantly beta-active Bi^{213} as shown below, rather than through the even-numbered elements as in the natural series.

Sometime later Turner¹⁶ predicted that U^{237} would be a beta rather than an alpha emitter and supported Meitner, Strassmann, and Hahn's³ assignment of a 25-day Pa activity to Pa^{233} . The decay scheme proposed by Turner was

Turner's scheme leads through elements 85 and 87, as did the prediction of Widdowson and Russell, but an emanation would not be formed in the main line. Feather¹⁷ believed Turner's predictions should be correct, and in actual fact the only deviation from our experimental findings is his prediction that the major decay of Bi^{213} would be by alpha emission, whereas this mode accounts for only 2 per cent of the disintegrations.

Ponisovsky,¹⁸ from independent studies of the regularities in the stable isotopes, predicted essentially the same series, with the difference that the Th^{229} was predicted to be beta active, leading to an alpha active Pa^{229} which would give the Ac^{225} without the appearance of a radium isotope in the chain.

With respect to possible alpha branching of the Ra^{225} , our experiments on separating this isotope from its daughter Ac^{225} have enabled us to set 0.5 per cent as an upper limit on the amount of such branching. No emanation has been detected. No evidence for beta decay of the Th^{229} has been found. The properties of the theoretical product, Pa^{229} , are known from material produced by cyclotron bombardment.¹⁹

2. EXPERIMENTAL WORK

U^{233} . The U^{233} used in these experiments was prepared by neutron irradiation of thorium in the uranium-graphite pile. Following decay of most of the intermediate Pa^{233} and Th^{233} , the uranium was separated by extraction with ether.²⁰ A series of extractions and precipitations of sodium uranyl acetate, ammonium diuranate, and uranyl peroxide served to give complete chemical and radiochemical purification of the uranium. The nuclear properties of this isotope are described elsewhere.²¹

The U^{233} prepared in this way contained 4 to 5 per cent of U^{238} since the thorium compounds irradiated normally contained around 1 ppm of natural uranium impurity. Account was taken of the UX activity introduced from this isotopic impurity in experiments involving thorium isotopes. Lower members of the uranium-decay chain were present in amounts which were insignificant because of the long half life of U^{234} and its low concentration.

An important impurity was found to be U^{232} (reference 22), which decays to radiothorium of 1.9-year half life, followed by $\text{ThX}(\text{Ra}^{224})$

and its short-lived daughters. The RdTh half life is so short relative to that of the Th^{229} that, even with only 1 disintegration of U^{232} in 5700 disintegrations of U^{233} (the concentration actually found in one sample of the material by a mica absorption method), a significant fraction of the daughter radioactivities extracted after a decay period of a few weeks or months is due to this impurity. The ratio of Th^{229} activity to RdTh activity was found to vary from about 2 to 3.5 for different samples of U^{233} . The origin of the U^{232} is probably a small Pa^{231} impurity in the irradiated thorium, since Pa^{231} has a high neutron capture cross section.²³ The capture product Pa^{232} decays to U^{232} by beta emission with a half life of 1.4 days.²² An alternative possibility is that there is a sufficient flux of fast neutrons to give a sufficient (n,2n) reaction with the thorium to yield the Pa^{231} . A second-order absorption would then give rise to the U^{232} .

3. ISOTOPIC ASSIGNMENTS

Assignments of the periods and radiations to definite isotopes were made on the basis of radiochemical separations together with range analyses of the alpha particles by means of a pulse analyzer.²⁴

The isolated thorium activity showed the anticipated alpha activity. After RdTh daughters had grown to equilibrium, alpha activity continued to grow over a period of time at a rate corresponding to a half life of the order of three weeks. The number of alpha activities growing from the Th^{229} was shown to be four, both from range analysis by the pulse analyzer and from the increase in alpha activity. Radiochemical isolation of a combined radium-actinium fraction (e.g., on barium sulfate) gives an alpha-active preparation into which two alpha activities grow with a 5-min half life, followed by growth with a $\frac{3}{4}$ -hr half life. Separation into radium and actinium fractions shows the radium isotope to possess a soft beta particle of about 0.2 Mev energy, while the actinium fraction repeats the alpha-activity growth pattern noted above. Four alpha activities (the actinium isotope and its daughters) grow into the radium fraction on a time relation that is dependent on the 14.8-day radium period and the 10.0-day actinium period. The fact that two alpha activities (and no beta) grow with a 5-min period indicates that the half life of At^{217} is considerably shorter than the 5-min period of Fr^{221} . This is borne out by the period determined from coincidence measurements (0.018 sec). A bismuth fraction free of lead isotopes shows an alpha activity and a beta activity decaying with the same half life, leaving a beta activity ascribable to daughter Pb^{209} . The short half life of the alpha emitter and the long range of its particle indicate that it is due to Po^{213} , produced

by beta decay of Bi^{213} . Evidence from range analysis of the Bi^{213} activity indicates some branching by alpha decay.

Th^{229} . This isotope, together with the radiothorium impurity mentioned above, was isolated from the purified U^{233} solution after a suitable period of time by coprecipitation with zirconium iodate.

One- to two-tenths of a milligram of zirconium nitrate and sufficient iodic acid solution to give a final iodate concentration of 0.05M were added per milliliter of solution of U^{233} in 0.1N nitric acid. The precipitated zirconium iodate was washed by centrifugation, dissolved in sulfur dioxide-water mixture, heated to remove liberated iodine, and diluted; and the zirconium was reprecipitated with iodic acid. Four to five of these cycles served to decontaminate completely from uranium, radium, and most of the actinium. Bismuth and lead activities were removed by one or two lead sulfide by product precipitates.

In order to prepare samples sufficiently free from carrier for alpha-particle range measurements in the pulse analyzer and to remove any traces of actinium activity, the following procedure was used. The thorium isotopes were coprecipitated from the final zirconium iodate solution with lanthanum fluoride carrier (0.1 to 0.2 mg/ml), the fluoride precipitate was metathesized to hydroxide with concentrated potassium hydroxide, and the hydroxide was dissolved in 0.05 nitric acid. Separation of the thorium activity from the lanthanum carrier was accomplished by extraction with a solution of 0.15M thenoyltrifluoroacetone (TTA)²⁵ in benzene. The change from zirconium to lanthanum carrier was necessary since the former extracts into TTA solution under the conditions used, whereas the latter does not. In some cases TTA extraction of the thorium isotopes was made directly from the uranium solution. The TTA-benzene solution was in either case evaporated directly on the counting plate or reextracted with 8N nitric acid, and the latter solution was evaporated. Ignition of the resulting plates left an essentially weightless film of the thorium activity.

Since the Th^{229} half life is several thousand years, indirect methods of determining this property were necessary. A known amount of freshly purified U^{233} was allowed to decay for a measured time. UX_1 tracer was then added and the thorium activity isolated as above. The UX_1 tracer provided a means of determining the yield of thorium through the separation procedure without introducing any foreign alpha activity. The ratio of Th^{229} to radiothorium was determined by alpha-pulse analysis. If corrections were applied for yield and for radiothorium impurity, the amount of Th^{229} activity which had grown into the U^{233} could be calculated, and from this the Th^{229} half life. The mean value obtained from eight such determinations was 7340 ± 160 years.

The alpha radiations of Th^{229} have been found to be complex. The main group of alpha particles, which constitutes approximately 10 per cent of the total, has an energy of 4.85 ± 0.01 Mev. Two small longer-range groups of particles have been resolved from the main group, differing from it by 90 and 170 Kev, respectively. The less energetic of these two small groups contains roughly about twice the number of alpha particles in the other. Figure 2 is a typical curve obtained with the pulse analyzer of the thorium activity which shows the two longer-range groups of the Th^{229} alpha particles together with the RdTh impurity mentioned above. The energy of the Th^{229} particles was determined by placing a standard containing some Po^{210} (5.30 Mev) and Io (4.66 Mev)²⁶ in the chamber together with the sample. The Th^{229} energy was found by interpolation from the resulting calibration curve using the Po^{210} , Io , and RdTh peaks²⁷ as reference points of known energy.

Ra^{225} . The Ra^{225} (and ThX from the U^{232} impurity) was isolated from the U^{233} solution from which the thorium activity had been separated. Both barium sulfate and barium chloride were used as carriers for the radium activity; the latter was found to be preferable with regard to decontamination from actinium. With barium chloride the procedure was to add 1 mg of barium as nitrate to the U^{233} solution, reduce the volume to a few tenths of a milliliter, and add seven times the volume of hydrochloric acid-ether solution (6 parts conc. HCl to 1 part ethyl ether). After cooling with ice the precipitated barium chloride was centrifuged and reprecipitated in the same manner. Two or three precipitations were sufficient to remove the U^{233} ; however, appreciable actinium activity still remained at this point. This was removed either by precipitating lanthanum fluoride from the solution or by adding lanthanum nitrate, evaporating to dryness, and extracting the lanthanum and actinium nitrates with absolute ethyl alcohol. Lead sulfide was precipitated from the solution to remove bismuth and lead activity, and the barium was finally precipitated and mounted for counting as the sulfate.

Because of the low energy of its beta particles, the half life of the Ra^{225} was determined indirectly by following the growth and decay of the alpha activity in the fraction isolated as above. Figure 3 shows an experimental curve (solid line) and theoretical curves (broken lines) calculated on the basis of a 10.0-day Ac^{225} daughter (see below) assuming different values for the Ra^{225} half life and using the observed maximum count. The growth of the alpha activity does not follow precisely the theoretical values owing to the presence of the ThX impurity. However, by the time the maximum value has been passed the short-lived ThX has largely decayed away. The experimental points

best fit a theoretical curve for a 14.8-day radium half life. Since the Ra^{225} and Ac^{225} half lives are similar, transient equilibrium is approached very slowly, and direct determination of the Ra^{225} half life from the decay curve, with reasonable accuracy, would be possible only after some hundreds of days of decay.

Beta-ray absorption curves were taken on samples of Ra^{225} re-purified after having been allowed to stand for some weeks in order to eliminate the effects of the ThX daughters. The original Ra fraction was isolated from the U^{233} solution upon barium chloride carrier and reprecipitated to remove uranium and thorium activities. After about 30 days the Ra^{225} was purified from daughter activities by the above procedure and mounted on platinum, and absorption curves were taken. Figure 4 is the curve of the absorption in mica obtained in a windowless Geiger-Mueller counter 5 hr after separation. One-half hour after separation this sample showed 30 alpha c/min. Other curves taken with a low-absorption counter using a thin (about 0.1 mg) Zapon window and aluminum absorbers were similar. The amount of Ra^{225} activity which should have been present initially was calculated from the growth of alpha activity in the sample to be about 650 c/min, making approximate corrections for counting geometry. This agrees well with the value for zero absorber extrapolated from the curve after correcting for back-scattering and self-absorption. Figure 5 shows the curve taken on another sample, 8 hr after separation, with an ordinary thin-window (3.3 mg/cm^2 of mica) Geiger-Mueller counter using Al absorbers. The absorption half thickness of the Ra^{225} beta particle from these curves is about 6 mg/cm^2 and the range about 35 mg Al per square centimeter, corresponding to an energy of approximately 0.2 Mev. No reliable information is available about gamma rays.

Ac^{225} . Ac^{225} was separated by means of lanthanum fluoride carrier from the U^{233} solution from which Th^{229} had been removed. The fluoride precipitate was metathesized by means of potassium hydroxide and then dissolved in nitric acid. After two or three such cycles barium nitrate was added to "hold-back" radium, the solution was evaporated to dryness, and the lanthanum and actinium were extracted from the residue with absolute ethyl alcohol.²⁸ The alcohol was evaporated, more barium nitrate was added, and the extraction was repeated. After precipitating lead sulfide to remove any bismuth or lead activity remaining, the lanthanum and actinium were precipitated as fluoride and mounted. A typical growth and decay curve for the Ac^{225} fraction is shown in Fig. 6, from which the half life of 10.0 days was obtained by least-squares analysis.

Fr^{221} . Analysis of the growth curves of the alpha activity in the Ac^{225} sample showed that three alpha activities grew in, two with a

half life of about 5 min followed by a third with a half life of about 45 min. The 5-min growth appeared to start with the flaming of the plate containing the activity, and after equilibrium had been reached the 5-min growth reappeared if the sample was reflamed. Experiments with Cs^{134} tracer indicated that this activity could be volatilized by flaming under similar conditions. These facts indicated that the Ac^{225} daughter, Fr^{221} , was an alpha emitter of about 5-min half life and its daughter was also an alpha emitter of much shorter life.

The half life of the Fr^{221} was determined more accurately by precipitating lanthanum hydroxide from a small volume of a solution of Ac^{225} and its daughters with ammonia, mounting the supernatant solution, and following the decay of the alpha activity obtained. Figure 7 shows the observed decay curve together with the curve resulting from subtraction of the nondecaying background (probably Ac^{225}). The half life obtained from the latter curve gave a value of 4.8 min.

At^{217} . The half life of At^{217} was determined by measuring the time interval between successive alpha-particle emissions by Fr^{221} and At^{217} . A sample of Ac^{225} was mounted on a very thin Zapon film supported on a 2-mil wire ring of about 1 cm diameter. The ring was placed in a vertical position on the bottom electrode of the chamber of a standard alpha counter.²⁹ A resistor and condenser in series were connected between the plate and cathode of one of the tubes of the first Eccles-Jordan trigger pair³⁰ in the scaling circuit of the counter. The voltage changes across the condenser were followed by an oscilloscope, the plates of which were connected directly across the condenser. Thus a single alpha particle would cause the electron beam of the oscilloscope to sweep across the screen at a rate that was dependent upon the time constant of the circuit. If two successive alpha particles were emitted within this time interval the beam would be returned to its original position and the distance through which it swept would be a measure of the interval between the pulses. The time constant of the circuit was such that 0.2 sec was required for the beam to sweep across the screen. The distances swept for successive emissions were observed visually. A detailed description of the circuit and method may be found in another paper from the Argonne National Laboratory.³¹

The purpose of the special mounting of the sample was to increase the geometry factor to approximately 100 per cent in order to obtain as high a ratio of coincident to single pulses as possible. A low counting rate (9 c/min) was used in order to reduce corrections for coincidences due to random emission of single particles. This correction varied linearly in the range of interest, from nil at zero time to about 3 per cent at 0.2 sec.

Figure 8 shows the integral curve obtained by plotting the total number of coincidences within a given time interval against the time interval. The mean interval was 0.026 sec, from which was obtained the value 0.018 sec for the half life of At^{217} . The same half life was obtained by graphical analysis (see Fig. 9). Essentially all the coincidences were observed within the maximum time interval. By plotting the difference between the total number of coincidences and the number within a given time interval against the interval on semi-logarithmic paper, a straight line was obtained, the slope of which determined the half life of At^{217} .

Bi^{213} . The Bi^{213} was isolated from a solution of Ac^{225} by precipitation with bismuth sulfide carrier. Four or five cycles consisting of solution of the sulfide in hot concentrated hydrochloric acid, dilution with water, and reprecipitation of bismuth with hydrogen sulfide served to remove all except lead activity, which was separated upon lead sulfate precipitates.

The Bi^{213} half life was determined by following the very short-lived alpha-emitting daughter Po^{213} rather than the beta particles of Bi^{213} itself since the growth of beta particles of 3.3-hr Pb^{209} is a complicating factor in the latter case. Figure 10 shows a sample decay curve of the Bi^{213} fraction which, after subtracting the nondecaying counter background, gives a value of 47 min for the Bi^{213} half life. This same isotope has been identified as a decay product of Pa^{229} by other workers at Argonne National Laboratory.¹⁹

Absorption curves in aluminum of the beta particles from Bi^{213} and Pb^{209} were taken with samples of Ac^{225} in equilibrium with its daughters. Figure 11 shows an experimental curve which has been resolved into the two components; the beta particles of Bi^{213} have a half thickness of 54.7 mg/cm² of Al, corresponding very roughly to an energy of 1.2 Mev, and those of Pb^{209} have a half thickness of 14.7 mg/cm², corresponding approximately to the reported value of 0.7 Mev.¹

4. ENERGIES OF ALPHA PARTICLES OF Ac^{225} , Fr^{221} , At^{217} , AND Po^{213}

The energies of the alpha particles of these isotopes were determined with the pulse analyzer using a standard of RdTh and its daughters, whose energies are known, to establish reference points. The instrument²⁴ which was used has 48 electronic channels which register all the alpha pulses within a narrow energy band; the 48 channels cover 48 contiguous energy bands of equal width increasing in energy from channel 1 to channel 48. By plotting the total number of alpha counts per channel against channel number, a peak will be observed for each

alpha group. The position and size of the peak measure, respectively, the energy and abundance of the alpha group. [We are indebted to B. Weissbourd and J. Mech for assistance with the pulse analyses of the numerous samples.]

The values obtained for the energies of the alpha particles were 5.80 ± 0.05 Mev for Ac^{225} , 6.30 ± 0.05 Mev for Fr^{221} , 7.00 ± 0.05 Mev for At^{217} , and 8.34 ± 0.01 Mev for Po^{213} . A small peak containing about 25 to 30 per cent of the number of alpha particles in the main peaks was observed at 6.05 Mev; this has been attributed tentatively to fine structure in the Fr^{221} spectrum. Figure 12 is a typical pulse-analyzer curve showing this small peak together with the large peaks for Ac^{225} , Fr^{221} , and At^{217} . It is improbable that this activity is due to unrecognized branching in the series. No radiochemical evidence has been found for branching decay of Th^{229} , Ac^{225} , Fr^{221} , or At^{217} . Systematics of decay of the heavy elements³² suggest that At^{217} and Fr^{221} may not be beta stable. There is also the suggestion that At^{217} may have an as yet unobserved alpha group of higher energy.

Bi^{213} does exhibit some branching decay. The bismuth activity from a solution of Ac^{225} was separated with lead sulfide carrier and purified from other activities by repeated sulfide precipitations. The lead was then precipitated as sulfate, and the supernatant containing the carrier-free bismuth activity was mounted and examined in the pulse analyzer. In some cases plates were prepared by direct electrodeposition of the bismuth from 1N HCl solution of the actinium. In addition to the normal peak of Po^{213} at 8.34 Mev a small peak at about 6.0 Mev was observed. The sample was followed for a period of several half lives, and both peaks decayed with the Bi^{213} half life of 47 min. The number of alpha particles in the shorter-range peak was 2.0 ± 0.2 per cent of the total in both, based on 15 determinations. An experimental curve is shown in Fig. 13. Although the energy of this small peak is close to that attributed above to Fr^{221} , the number of alpha particles from the Bi^{213} is insufficient to account for more than a fraction of the total in that peak.

With the quantities of material available at the time of these experiments, attempts to isolate the Tl^{209} activity were unsuccessful. Since then Hagemann³³ has been able to characterize the isotope as decaying with a 2.2-min half life by emission of a 1.8-Mev beta particle. Gamma rays if present constitute a maximum of 1 per cent of the Geiger-Mueller activity.

Table 1

Isotope	Type of radiation	Half life*	Energy of radiation, Mev
Np ²³⁷	α	2.20×10^6 years (ref. 10)	4.77
Pa ²³³	β^-	27.4 days (ref. 4)	0.23 (ref. 11)
U ²³³	α	$1.62 \pm 0.01 \times 10^5$ years (ref. 12)	4.80 (ref. 13)
Th ²²⁹	α	$7.34 \pm 0.16 \times 10^3$ years	4.85 (~70%) 4.94 (~20%) 5.02 (~10%)
Ra ²²⁵	β^-	14.8 ± 0.2 days	~0.2
Ac ²²⁵	α	10.0 ± 0.1 days	5.80
Fr ²²¹	α	4.8 ± 0.1 min	6.30
At ²¹⁷	α	0.018 ± 0.002 sec	7.00
Bi ²¹³	β^- (98%); α (2.0%)	47 ± 1 min	~1.2 (β^-); 6.0 (α)
Po ²¹³	α	Very short	8.34
Tl ²⁰⁹	β^-	2.20 ± 0.07 min	1.8
Pb ²⁰⁹	β^-	3.3 hr (ref. 1)	0.7 (ref. 1)
Bi ²⁰⁹	Stable		

*Limits of error for Ra²²⁵, Ac²²⁵, Fr²²¹, and At²¹⁷ are estimates rather than true probable errors.

ELEMENT AND ATOMIC NUMBER

Fig. 1 — Decay scheme of the neptunium series.

Fig. 2—Pulse-analyzer curve of thorium alpha activity showing the three alpha peaks of Th^{229} together with the peaks due to RdTh impurity.

Fig. 3—Growth and decay of alpha activity from Ra^{225} preparation. Theoretical decay curves calculated on the basis of 10-day Ac^{225} and 15- and 14.8-day Ra^{225} are shown by the broken lines.

Fig. 4—Absorption of Ra^{225} beta particles in mica.

Fig. 5—Absorption of Ra^{225} beta particles in aluminum measured with a mica window Geiger-Mueller tube (3.3 mg/cm² of mica).

Fig. 6—Growth and decay of alpha activity from Ac^{225} .

Fig. 7—Decay of alpha activity from Fr^{221} . The long-lived background is probably unseparated Ac^{225} .

Fig. 8—Integral curve obtained by plotting the total number of coincidences observed between Fr^{221} and At^{217} alpha particles in fixed time intervals against the time intervals. Corrections for chance coincidences have been applied.

Fig. 9—Graph of the difference between asymptotic value of the total number of observed coincidences (from Fig. 8), N_{∞} , and the number observed within a fixed interval, N_t , against the time interval. The slope of the line gives the half life of At^{217} directly.

Fig. 10—Decay of alpha activity from Bi²¹³ and daughters.

Fig. 11—Absorption curve in aluminum of beta particles from Ac²²⁵ and daughters showing the two components due to Pb²⁰⁹ and Bi²¹³.

Fig. 12—Typical pulse-analyzer curve of the alpha particles from Ac²²⁵ and daughters.

Fig. 13 — Pulse-analyzer curve of alpha particles from Bi^{213} and daughters. The small peak at 6.0 Mev containing 2 per cent of the total alpha particles is due to alpha branching of Bi^{213} .

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Paper 1.5

FAST-NEUTRON FISSION OF U^{233} , Pa^{231} , AND Pu^{239}

By Gerhart Friedlander, John W. Gofman, and Glenn T. Seaborg

[Editor's Note: Contribution from the University of California Radiation Laboratory, Berkeley. Based on Report CF-221. Prepared for publication Aug. 5, 1942.]

ABSTRACT

Relative cross sections determined in this investigation are: Pu^{239} , 1.5 ± 0.5 ; U^{233} , 1.8 ± 0.5 ; U^{238} , 0.4 ± 0.1 ; U^{235} , 1; and Pa^{231} , 0.9 ± 0.3 .

We have measured the relative cross sections for the fission of Pu^{239} , U^{233} , U^{235} , U^{238} , and Pa^{231} by the fast neutrons from a radium-beryllium source. Although the neutrons from a radium-beryllium source have a rather wide distribution in energy, the cross sections for such neutrons are of some interest because various measurements¹ have shown that this energy distribution is not far different from that of the neutrons produced in the fission process. These measurements, which were made several months previous to the time of writing, must be regarded as preliminary since they were made on rather small samples.

In the measurements, the samples were placed on one electrode of an ionization chamber connected to a four-stage linear amplifier and recording system which was adjusted so as to record the pulses due to fissions. The neutron source consisted of a mixture of 1 g of radium (as bromide) with 5 g of beryllium powder in a double-walled monel container. The ionization chamber was cadmium-lined, and both it and the first stage of the amplifier were surrounded by cadmium and boron carbide shields. The entire assembly was mounted on a steel table in the absence, as far as possible, of hydrogenous

material. A cadmium disk was interposed directly between the sample measured and the neutron source. A cross section of the apparatus used, drawn to scale, is shown in Fig. 1. The constancy of the gain of the amplifier was checked between successive measurements by measuring the fission rate of a thin uranium sample.

Following is a description of the samples upon which the measurements were performed.

1. A sample containing $0.5 \mu\text{g}$ of Pu^{239} was isolated² from neutron-bombarded uranyl nitrate hexahydrate $[\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and was present in a thin layer of rare earth-fluoride carrier material (thickness of about $300 \mu\text{g}/\text{cm}^2$). The weight of Pu^{239} in the sample was determined from its alpha-counting rate, as measured with an alpha-counting ionization chamber of calibrated efficiency, together with its half life (30,000 years).

2. A sample containing $3.8 \mu\text{g}$ of U^{233} was isolated³ from neutron-bombarded thorium nitrate and was electrolytically deposited with a thin layer of extraneous material (thickness of about $300 \mu\text{g}/\text{cm}^2$). The weight of U^{233} in the sample was determined from its alpha-counting rate, together with its half life³ (1.2×10^5 years).

3. A sample of enriched U^{235} containing $1.3 \mu\text{g}$ of U^{235} , $5.2 \mu\text{g}$ of U^{238} , and $0.0014 \mu\text{g}$ of U^{234} was present in a thin layer of extraneous material (thickness of about $300 \mu\text{g}/\text{cm}^2$). The isotopic analysis⁴ was performed by J. W. Kennedy.

4. A sample of ordinary uranium, i.e., uranium containing its natural abundance of isotopes, weighed $200 \mu\text{g}$ and occupied an area of about 1.3 cm^2 . It was prepared by electrolytic deposition from uranyl nitrate dissolved in absolute alcohol, and its weight was calculated from its alpha activity and the half life of uranium.

5. A sample of Pa^{231} weighing $1.04 \mu\text{g}$ was present in a thin layer of extraneous matter (thickness of about $300 \mu\text{g}/\text{cm}^2$), and its weight was calculated from its alpha-counting rate and the half life of Pa^{231} (3.2×10^4 years).

The results of the measurements are summarized in Table 1. The errors listed in the last column are the standard deviations calculated from the total number of counts in the usual manner.

From the counting rate ($3.5 \pm 0.4 \text{ c/hr}$) and the composition ($1.3 \mu\text{g}$ of U^{235} + $5.2 \mu\text{g}$ of U^{238}) of the enriched U^{235} sample, together with the counting rate ($80.5 \pm 4.5 \text{ c/hr}$) and the composition ($198.6 \mu\text{g}$ of U^{238} + $1.4 \mu\text{g}$ of U^{235}) of the natural uranium sample, it is possible to calculate the counting rate due to U^{235} alone and U^{238} alone. In this manner there is obtained for U^{235} a fast-neutron fission-counting rate of $1.1 \pm 0.3 \text{ c/hr}/\mu\text{g}$ and for U^{238} a rate of $0.4 \pm 0.02 \text{ c/hr}/\mu\text{g}$. These results

are included in Table 2, in which there are listed the fast-neutron fission-counting rates per microgram for the five isotopes Pu^{239} , U^{233} , U^{235} , U^{238} , and Pa^{231} , together with their fast-neutron fission cross sections relative to U^{235} .

It should be pointed out that the relatively low value for the cross section of U^{238} is probably due to the fact that only a fraction of the radium-beryllium neutrons have an energy above the energy threshold for the fission of U^{238} . It was thought interesting to include the nucleus Pa^{231} in the measurements because this nucleus, like U^{238} , does not undergo fission with thermal neutrons but has an energy threshold for fission much nearer the thermal region than that of U^{238} .

One source of error in these measurements is the variation in the thickness of the various samples. Another is the slightly nonuniform distribution of material which is shown in the individual samples. The fact that the various sample plates were not of the same area need introduce no error provided the neutron density is constant over the whole sample, since none of the samples are thick enough to absorb any appreciable fraction of the neutrons incident upon them. From Fig. 1 it can be seen that the neutron density should be fairly constant over the area of the samples.

In the analysis of these fast-neutron measurements, we have made no attempt to estimate uncertainties in the weights of the various samples.

Another source of error arises from the possibility that slow neutrons might be leaking through to the sample in spite of the shielding with cadmium and boron. However, we were able to show that the fission-counting rate due to any such slow neutrons was very small compared with the fission-counting rate due to the fast neutrons. The following method was employed in which the 3.8- μg U^{233} sample, because of its relatively high fission rate with slow neutrons, was used for the test for the possible effect of slow neutrons.

In an experiment with the apparatus and neutron source as described above, this sample gave a fission-counting rate of 6.8 ± 0.8 c/hr. (The slight difference between this value and the counting rate of 7.7 ± 0.5 c/hr reported above is due to a small change in the gain of the amplifier.) When the apparatus was surrounded as completely as possible by a large amount of paraffin, for the purpose of increasing the number of slow neutrons in the vicinity of the ionization chamber, the fission-counting rate increased by only a very small amount, namely, to 8.7 ± 0.8 c/hr. This experiment of counting with and without paraffin was then repeated with a second apparatus which was identical with the first except that there was absolutely no cadmium-boron

shielding. All other geometrical conditions, such as position of the neutron source, etc., were maintained identical with those used in the fast-neutron measurements outlined above. With this apparatus a counting rate of 7.8 ± 1.5 c/hr was obtained with no paraffin present, and this increased to 47 ± 5 c/hr when the apparatus was surrounded by the same large amount of paraffin. An analysis of these results shows that not more than a few per cent of the fission counts obtained with the cadmium-boron-shielded chamber are due to slow neutrons.

ACKNOWLEDGMENT

We are indebted to J. W. Kennedy for the sample of enriched U^{235} and for the isotopic analysis of this sample.

Table 1—Summary of Counting Rates in Fast-neutron Fission Experiments

Sample	Total hours	Total counts	Counts per hour
0.5 μg Pu^{239}	51.2	41	0.80 ± 0.12
3.8 μg U^{233}	31.5	242	7.7 ± 0.5
1.3 μg U^{235} + 5.2 μg U^{238}	25.0	88	3.5 ± 0.4
198.6 μg U^{238} + 1.4 μg U^{235}	4.08	329	80.5 ± 4.5
1.04 μg Pa^{231}	27.2	27	1.0 ± 0.2

Table 2—Relative Fast-neutron (Ra-Be) Fission Cross Sections

Isotope	Fission rate, c/hr	Weight, μg	Fission rate per μg , c/hr	Relative cross section*
Pu^{239}	0.80 ± 0.13	0.5	1.6 ± 0.3	1.5 ± 0.5
U^{233}	7.7 ± 0.5	3.8	2.0 ± 0.1	1.8 ± 0.5
U^{238}	77 ± 4.5	193.4	0.4 ± 0.02	0.4 ± 0.1
U^{235}	1.4 ± 0.4	1.3	1.1 ± 0.3	1
Pa^{231}	1.0 ± 0.2	1.04	1.0 ± 0.2	0.9 ± 0.3

* Standard deviations given do not include uncertainties in the weights of the samples.

Fig. 1 — Fast-neutron apparatus.

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Paper 1.6

ABUNDANCE OF U^{238} IN SAMPLES OF U^{233}

By Winfred Rall and Arthur J. Dempster

[Editor's Note: Contribution from the Metallurgical Laboratory, University of Chicago. Based on Report CP-3530. Prepared for publication June 6, 1946.]

1. INTRODUCTION

Two samples of U^{233} prepared by L. I. Katzin and G. T. Seaborg have been examined with the mass spectrograph in order to determine the amount of U^{238} impurity that they contained. The samples had been prepared by extracting uranium from thorium which had been irradiated by neutrons. The U^{233} thus extracted contained some ordinary uranium, mostly U^{238} , which had been present in the thorium as an impurity. In order to deduce the nuclear properties of the U^{233} , it was thus necessary to know how much U^{238} was present.

Photographs with a similar sample clearly showed the two isotopes and indicated that the U^{238} amounted to approximately 4 per cent (see Fig. 1). The amount is thus too small for accurate photometric measurement, and the ratio of the two isotopes was finally measured by comparing the ions electrically. The samples amounted to about 1 mg of the tetrafluoride, of which a large part was recovered.

2. SOURCE

A spark between solid electrodes was used as a source of ions, and the analyzed isotopes were collected simultaneously.

Adjustments were made with the electrode in Fig. 2(a).

The two silver isotopes at masses 107 and 109 were made to fall symmetrically on the two collecting slits, and then the electric fields were altered by the exact amount required to bring the doubly charged

uranium ions at masses 116.5 and 119 on to the collecting slits, which had the exact separation required for these masses. The two electrodes, shown in Fig. 2, were held in a magazine and could be removed and interchanged in a few minutes by means of the sylphon and Wilson seal adjustments without opening the system or altering the magnetic field.

3. SECONDARY ELECTRONS

To avoid secondary electrons from the collectors, the electrode arrangement shown in Fig. 3 was first tried. This is similar to an arrangement previously used by A. O. Nier in the analysis of gas ions.

The "repeller" electrode R is charged negatively to keep secondary electrons back on the collectors A and B. Tests were made with normal UF_4 , and it was found that 96 per cent of the U^{238} beam passed through the 0.75-mm slit in A to the collector B under good vacuum conditions. With the U^{233} sample, however, the scattered ions could be more accurately measured in the symmetrical arrangement shown in Fig. 4 by moving the 233 beam over into the B collector and measuring the scattered ions in A. The deep collectors of Fig. 4 were therefore used for the final measurements. The diaphragm R was sometimes charged to -45 volts but had little influence on the ratio.

4. ION COMPARISONS

The ratio of the two isotopes was measured by comparing the charges collected in A and B by means of the circuit shown in Fig. 5. The two electrometers E_1 and E_2 were Lindemann Electrometers made in the Metallurgical Laboratory Central Shop. The charges collected in A and B were exactly compensated by equal and opposite induced charges, whose ratio was fixed by the settings on the four-dial resistance boxes R_1 and R_2 . The ratio of the ions collected is computed from the resistances R_1 and R_2 and the measured capacity ratio of the collecting systems.

5. OBSERVATIONS

The observed ratio of the ions must be corrected for background and for scattering from the main 233 bundle into the 238 collector. Observations with normal uranium showed that this amounted to approximately 0.5 per cent. This makes an important correction to the faint 238 isotope, which was itself approximately only 4 per cent of the 233 isotope. The correction in each case was deduced by observing the silver ions collected in B when the silver isotope at 109

falls in collector A. The data for three sets of observations on different days are given in Table 1. The first column gives the number of independent measurements of the values in column 2.

The most probable value for the percentage of U^{233} in the sample was 96.35. Approximately 0.6 mg of tetrafluoride was used in these measurements, and most of this was recovered.

An earlier sample that had been used by H. L. Anderson and A. N. May¹ had been measured without corrections for scattered ions and had given 95.8 per cent of U^{233} and 4.2 per cent of U^{238} . It was only later that the importance of scattering was discovered. If we make the same correction for scattering as in the case described above, we obtain approximately 96.4 per cent for U^{233} and 3.6 per cent for U^{238} in the May-Anderson sample.

Photometric measurements may be used to verify an estimate, at the expense of shifting the responsibility for the accuracy to the chemists. This was done in the case of the May-Anderson sample. To 0.25 mg of the sample, a carefully weighed amount of ordinary uranium equal to three-fourths of 0.25 mg was added by F. Hagemann of L. I. Katzin's group. If the ratio of U^{233} to U^{238} had been 7 to 1, as at first estimated from photographs of the isotopes, by this addition U^{238} would have been brought up to exact equality with the U^{233} . Photometric measurements of the two isotopes, however, showed that the U^{238} was still distinctly weaker than U^{233} in the ratio of 45 to 55, indicating that the original amount had been present in the ratio of 1 to 25 in place of the estimated 1 to 7. This gives about 96 per cent for the purity of the U^{233} . Later this was determined electrically to be 96.4 per cent.

The accuracy obtained in the direct electrical measurements given in Table 1 is considered superior to the photometric measurements.

Table 1—Ratio of U^{238} to U^{233}

Number	Observed U^{238}/U^{233} ratio	Background	Corrected U^{238}/U^{233} ratio	Percentage of U^{233}
4	0.0462 ± 0.002	0.0066	0.040 ± 0.002	96.2 ± 0.4
3	0.0445 ± 0.002	(0.007)	0.0375 ± 0.002	96.4 ± 0.4
5	0.041 ± 0.002	0.005	0.036 ± 0.002	96.5 ± 0.4
Average				96.35

Fig. 1—Impurities in U^{233} sample. This is an early sample in which the separation of the uranium from the thorium was not complete. The thorium mass at 232 is approximately the same intensity as the uranium-233 isotope.

(a)

(b)

Fig. 2—Solid electrodes used as a source of ions.

Fig. 3—Ion collector.

Fig. 4—Ion collector.

Fig. 5— Ion-comparison circuit diagram.

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Paper 2.1

SPONTANEOUS-FISSION RATE OF U^{234}

By John W. Gofman and Glenn T. Seaborg

[Editor's Note: Contribution from the University of California Radiation Laboratory, Berkeley. Based on Report CF-220. Prepared for publication Aug. 7, 1942.]

ABSTRACT

A spontaneous-fission rate of zero counts in 420 hr corresponds to a half life of 10^{13} years for U^{234} .

Since in a number of the isotope-separation methods the U^{235} and U^{234} will occur together, it is important to obtain information on the spontaneous-fission rate of U^{234} . We have made a search for spontaneous fission in U^{234} . The result, zero counts in 420 hr, indicates that the spontaneous-fission rate corresponds to a half life for this process of more than 10^{13} years.

The sample of U^{234} which was used had a weight of $0.4 \mu\text{g}$ and was isolated from uranyl nitrate hexahydrate $[\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ by Fontana and coworkers,¹ using a modification of a method which has already been described. In this method the UX_1 is removed from the major portion of the uranyl nitrate by ether extraction and then precipitated as the fluoride with rare earth carrier material, after which the UX_1 is separated from the major portion of the rare earths by a modification of the iodate method of Noyes and Bray.² After the major portion of the UX_1 has decayed to U^{234} , the UX_1 which has not decayed is separated, together with rare earth fluoride, and the U^{234} is finally deposited onto platinum in a very thin layer by an electrolytic procedure. The final sample is present with an entirely negligible amount (about $300 \mu\text{g}/\text{cm}^2$) of extraneous material.

The weight of U^{234} in the sample used in our experiment was determined from its alpha-counting rate, as measured with a calibrated alpha-counting ionization chamber, together with the known half life of U^{234} (2.7×10^5 years).

The sample of U^{234} was placed on one electrode of a cadmium-shielded ionization chamber connected to a linear amplifier and recording system, adjusted so as to count the impulses due to fissions. The apparatus was tested periodically at intervals of 24 hr by replacing the U^{234} sample with a thin ordinary uranium sample and demonstrating that the fissions induced in this uranium by a neutron source were being recorded with the proper efficiency. It was shown, by considering the geometry of the ionization chamber and by measuring the variation with amplifier gain of the neutron-induced uranium fission-counting rate, that the over-all efficiency of the apparatus for recording fissions amounted to about 78 per cent.

The 0.4- μ g sample of U^{234} was counted in this apparatus for a total of 420 hr with a result of zero spontaneous-fission counts. Therefore, with the over-all efficiency of 78 per cent, the effective counting interval was 328 hr.

Table 1 indicates the probable half life of the spontaneous fission of U^{234} as calculated from the experimental result of zero fission counts in 328 hr as obtained with this 0.4- μ g sample. The probability that zero counts would be observed in 328 hr of counting, corresponding to the half life listed in the table, is given by $p = e^{-m}$, where m is the average number of counts to be expected for 0.4 μ g of U^{234} during the 328-hr interval.

Table 1—Probable Half Life of U^{234}

Half life of U^{234} toward spontaneous fission, years	Expected no. of counts in 328 hr for 0.4 μ g of U^{234}	Probability that zero counts would be observed
5×10^{12}	5.4	0.005
1×10^{13}	2.7	0.07
2×10^{13}	1.3	0.27
3×10^{13}	0.9	0.41

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Paper 2.2

FURTHER SEARCH FOR SPONTANEOUS FISSION IN U^{234}

By C. Blanchard, John W. Gofman, and Glenn T. Seaborg

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ABSTRACT

A search has been made for spontaneous fission of U^{234} , using a sample weighing 13 μg . The result, zero counts in 347 hr, indicates that the spontaneous-fission rate corresponds to a half life for this process of more than some 5×10^{14} years. In fact, this result leads to about a 50 per cent probability that the half life is more than 10^{15} years.

Since in a number of the isotope-separation methods the U^{235} and U^{234} will occur together, it is important to obtain information on the spontaneous-fission rate of U^{234} . We have made a search for spontaneous fission in U^{234} , and our results show that the rate for this process in this isotope is sufficiently low so that it will not be a source of trouble. In a previous experiment,¹ performed on a sample of much smaller weight, it had already been established that the half life for the process of spontaneous fission was more than some 10^{13} years.

The sample of U^{234} which was used had a weight of 13 μg and was isolated from uranyl nitrate hexahydrate $[\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ using a modification of a method which has already been described.² [The sample was prepared by B. J. Fontana, J. G. Hamilton, R. J. Prestwood, G. E. Sheline, and others.] In this method the UX_1 is removed from the larger portion of the uranyl nitrate by ether extraction and then precipitated as the fluoride with rare earth carrier material, after which the UX_1 is separated from the larger portion of the rare

earths by a modification of the iodate method of Noyes and Bray.³ After the major portion of UX_1 has decayed to U^{234} , the UX_1 which has not decayed is separated, together with rare earth fluoride, and the U^{234} is finally deposited in a very thin layer by an electrolytic procedure.

The weight of U^{234} in the sample used (13 μg) in our experiment was determined from its alpha-counting rate, as measured with a calibrated alpha-counting ionization chamber, together with the known half life of U^{234} (2.7×10^5 years). The exact sample thickness is not known. It is, however, a very uniformly spread sample with a thickness probably not greater than 1 mg/cm².

The sample of U^{234} was placed on one electrode of a cadmium-shielded ionization chamber connected to a linear amplifier and adjusted so as to count the impulses due to fissions. The apparatus was tested periodically by replacing the U^{234} sample with a thin ordinary uranium sample and demonstrating that the fissions induced in this uranium by a neutron source were being recorded with the proper efficiency. It was shown that the over-all efficiency of the apparatus for recording fissions amounted to 88 per cent.

The 13- μg sample of U^{234} was counted in this apparatus for a total of 437 hr with the result of zero spontaneous-fission counts. Therefore, with the over-all efficiency of 88 per cent, the effective counting interval was 305 hr.

In Table 1 the probable half life of U^{234} toward spontaneous fission as calculated from the experimental result of zero fissions in 305 hr is tabulated, neglecting any reduction in counting efficiency due to sample thickness. The probability that zero fissions would be observed in 305 hr is given by e^{-m} , where m is the expected number of fissions for this weight of U^{234} during the 305-hr interval.

Table 1 — Probable Half Life of U^{234}

Half life of U^{234} toward spontaneous fission, years	Expected no. of fissions in 305 hr for 13 μ g of U^{234}	Probability that zero fissions would be observed
1×10^{14}	8.2	0.00027
2×10^{14}	4.2	0.015
3×10^{14}	2.8	0.061
4×10^{14}	2.1	0.12
6×10^{14}	1.4	0.25
1.2×10^{15}	0.69	0.50

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Paper 2.3

TEST FOR SLOW-NEUTRON FISSION OF U^{234}

By C. Blanchard, Robert B. Duffield, John W. Gofman,
and Glenn T. Seaborg

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ABSTRACT

A sample of U^{234} (13.2 μ g as determined from its alpha-counting rate) was prepared by Fontana and coworkers by the method of extracting uranium-free UX_1 from uranium and allowing the UX_1 to decay to U^{234} . The slow-neutron-induced fission rate in this U^{234} sample was compared with that of a 1.33- μ g U^{235} sample (in 190 μ g of ordinary uranium). The results [$\sigma(\text{fiss}) U^{234} / \sigma(\text{fiss}) U^{235} = 0.002 \pm 0.001$] indicate that U^{234} does not undergo fission with slow neutrons with an appreciable cross section.

In a previous report Gofman, Duffield, and Seaborg¹ showed that the slow-neutron fission cross section of U^{234} was at most only 3 per cent of that of U^{235} . A new sample of U^{234} , containing 13.2 μ g of U^{234} as determined from the alpha-disintegration rate, has now been prepared by Fontana, Hamilton, Sheline, et al., by a method which has already been described.²

This U^{234} sample shows an alpha-disintegration rate of 167,000 per minute. Taking the U^{234} half life as 2.7×10^5 years, the weight of U^{234} in the sample is found to be 13.2 μ g. The sample, which has an estimated thickness of 1 mg/cm², is a uniformly spread electrolytic deposit containing some extraneous material.

The fission measurements were made with the same equipment and in the same manner described by Gofman, Duffield, and Seaborg.¹

The experimental data are given in Table 1.

$$U^{235} \text{ slow-neutron fission (c/hr}/\mu\text{g)} = \frac{64.7}{1.33} = 48.5$$

$$U^{234} \text{ slow-neutron fission (c/hr}/\mu\text{g)} = \frac{1.5 \pm 0.6}{13.2} = 0.11 \pm 0.05$$

$$\begin{aligned} \text{Relative cross section for slow-neutron fission} &= \frac{\sigma(\text{fiss}) U^{234}}{\sigma(\text{fiss}) U^{235}} \\ &= \frac{0.11 \pm 0.05}{48.5} = 0.002 \pm 0.001 \end{aligned}$$

The entire slow-neutron rate of the U^{234} sample could be accounted for by $4.4 \pm 1.7 \mu\text{g}$ of natural uranium impurity, assuming U^{234} does not undergo slow-neutron fission at all. We feel certain that this is the explanation for the very low observed counting rate and that U^{234} does not undergo fission with slow neutrons at all.

It is of interest to point out that, of the nuclei whose neutron-induced fission has been observed, those with an even number of neutrons (Io^{230} , Th^{232} , Pa^{231} , U^{238} , U^{234} , and Np^{237}) do not undergo fission with slow neutrons, and those with an odd number of neutrons (U^{233} , U^{235} , and Pu^{239}) undergo fission with slow neutrons. Apparently the larger amount of binding energy for the added neutron in the latter type of nuclei is an important factor in determining whether or not a nucleus is fissionable by slow neutrons. On this basis it appears unlikely, for example, that Np^{239} will undergo fission with slow neutrons.

Table 1

	Sample	Total hours	Total counts	Counts per hour
With paraffin but without cadmium shield	190 μg of natural uranium containing	59.2	5877	99.4
	1.33 μg of U^{235}			
	13.2 μg of U^{234}	44.5	355	$8.0 \pm 0.4^*$
With paraffin plus cadmium shield (0.35 g/cm^2)	190 μg of natural uranium	113.6	3946	34.7
	13.2 μg of U^{234}	37.2	241	$6.5 \pm 0.4^*$

*Errors estimated only for statistical fluctuations in fission counting. Sample thickness error or impurity errors not included.

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Paper 2.4

NEW ISOTOPES OF PROTACTINIUM AND URANIUM: Pa^{232} AND U^{232}

By John W. Gofman and Glenn T. Seaborg

[Editor's Note: Contribution from the University of California Radiation Laboratory, Berkeley. Based on Report CN-332. Prepared for publication Oct. 20, 1942.]

ABSTRACT

The bombardment of thorium with deuterons in the 60-in. Berkeley cyclotron produces, in addition to the 27.4-day Pa^{233} , the new isotope Pa^{232} , which emits beta particles and gamma rays with a half life of 1.6 days. The 1.6-day Pa^{232} decays to U^{232} , which emits alpha particles with a half life of about 30 years. The isotope U^{232} , which is formed in rather good yield (about 1 microcurie per 1000 $\mu\text{a-hr}$ of deuterons), will be useful as a tracer isotope for uranium and especially useful for tracing microgram and less than microgram amounts of uranium.

1. INTRODUCTION

It might be expected that the bombardment of thorium (single isotope, ${}_{90}\text{Th}^{232}$) with deuterons (about 14 Mev energy) in the 60-in. Berkeley cyclotron would result in the production of the isotope ${}_{91}\text{Pa}^{232}$ by the (d,2n) reaction in addition to the production of ${}_{90}\text{Th}^{233}$ by the (d,p) reaction and ${}_{91}\text{Pa}^{233}$ by the (d,n) reaction. Since the ${}_{91}\text{Pa}^{232}$ might decay to ${}_{92}\text{U}^{232}$, which could be very useful as a tracer isotope for uranium, this experiment was undertaken. It was found that the deuteron bombardment of thorium produces a 1.6-day beta- and gamma-emitting ${}_{91}\text{Pa}^{232}$, which decays to a 30-year alpha-emitting ${}_{92}\text{U}^{232}$.

2. EXPERIMENTAL PROCEDURE

A target of metallic thorium was bombarded with 500 μ a-hr of deuterons. After the bombardment, the protactinium was isolated chemically with the help of zirconium as a carrier. The thorium was digested for several hours with aqua regia, after which a fairly large fraction still remained undissolved, presumably because of thorium oxide present on the surface. The solid residue was taken up in 18N sulfuric acid and fumed for several hours to convert the thorium oxide into the sulfate, which then dissolved completely upon dilution of the acid to 3N. Zirconium nitrate was then added to both the aqua regia and sulfuric acid fractions, and the protactinium was separated by two successive zirconium phosphate precipitations from each fraction. The zirconium phosphate precipitates containing the protactinium were washed with 6N hydrochloric acid and then dissolved in 6N hydrofluoric acid. A small amount of thorium fluoride which had coprecipitated with the zirconium phosphate precipitated at this point and was centrifuged out. The hydrofluoric acid solution which contained the protactinium was cooled to 0°C and poured into an excess of ice-cold 4N sodium hydroxide. The resulting zirconium hydroxide precipitate, which contained protactinium hydroxide, was centrifuged out and dissolved in 4N nitric acid.

At this stage in the chemical procedure, the amount of zirconium carrier was reduced by carrying out a fractional precipitation of zirconium iodate. More than 96 per cent of the protactinium radioactivity was concentrated in the first 10 per cent of the zirconium precipitated as the iodate.

The zirconium iodate was dissolved in 9N hydrochloric acid, and a second phosphate-hydrofluoric acid-sodium hydroxide cycle was carried through. The final zirconium hydroxide precipitate, containing the protactinium hydroxide, was dissolved in a mixture of hydrochloric, nitric, and sulfuric acids and evaporated to dryness to convert it to the sulfate. The dried zirconium sulfate, 36 mg in weight, was dissolved in 30 cc of 0.3M ammonium fluoride solution, the pH was adjusted to the methyl red end point, and the solution was electrolyzed for about 10 hr using a copper cathode. In this procedure, with about 16 volts across the electrodes and about 110 ma current, the protactinium is deposited quantitatively, leaving the zirconium in solution.

The decay of this sample was followed with a Lauritsen quartz-fiber electroscope, with and without lead absorbers. An analysis of the decay curve showed, in addition to the 27.4-day Pa^{233} , a beta- and gamma-emitting activity of 1.6-day half life, which presumably was due to

Pa^{232} formed in the reaction $\text{Th}^{232}(\text{d},2\text{n})\text{Pa}^{232}$. Since the 1.6-day Pa^{232} emits beta particles, the daughter must be U^{232} . The growth of alpha particles due to U^{232} was observed in the sample by using an alpha-counting ionization chamber and linear pulse amplifier together with a magnetic field to bend out the very strong beta-particle background radiation. The growth curve indicated a half life of 1.6 days for the parent activity, as was to be expected.

The possibility existed that the alpha-particle emitter was actually Np^{232} or Pu^{232} formed by short-lived successive beta decays from Pa^{232} . This possibility was disproved by showing that the activity did not behave chemically like Np or Pu, but rather like uranium. Therefore one may be sure that the alpha emission is due to the isotope U^{232} .

It is interesting to note that ${}_{92}\text{U}^{232}$ must be the parent of ${}_{90}\text{RdTh}^{228}$, radiothorium. Radiothorium emits alpha particles with a half life of 1.90 years, and there are four other relatively short-lived alpha-particle emitters among the short-lived activities which follow in the decay chain to stable ${}_{82}\text{Pb}^{208}$. This means that after the complete decay of Pa^{232} into U^{232} , alpha-particle activity must continue to grow at a relatively slow rate (corresponding to a 1.9-year daughter) in the U^{232} sample. Observation over a period of 75 days showed that the alpha-particle activity in the U^{232} sample continued to grow at just the rate calculated for the growth of radiothorium (together with its decay products).

Since U^{232} is too long-lived to readily follow its decay, its half life can best be evaluated by using the measured value of the intensity of the beta particles of the 1.6-day Pa^{232} , together with the corresponding measured value of the intensity of alpha particles from the daughter U^{232} . In order to do this, the Lauritsen electroscope should be calibrated in an absolute manner for the Pa^{232} beta radiation, so that the electroscope reading can be converted into radioactivity intensity units (for example, microcuries). Since the electroscope was not calibrated for Pa^{232} radiation, a rough answer could be obtained by assuming that the efficiency of the electroscope is the same for Pa^{232} radiation as it is for Pa^{233} radiation, for which the electroscope had been calibrated in previous work. In this manner it was found that 0.12 millicurie of Pa^{232} beta radioactivity decayed to 0.016 microcurie of U^{232} alpha activity. These data lead to a value of about 30 years for the half life of U^{232} .

3. YIELDS

Our thick-target yield data are probably worth discussing even though they are rather rough. The relative yield of Pa^{232} to that of

Pa^{233} gives the yield of the (d,2n) reaction relative to the sum of the (d,n) and (d,p) reactions. [The (d,p) reaction gives the 23.5-min Th^{233} , which decays to Pa^{233} .] In the thorium-plus-deuterons bombardment, the value of about 0.4 was obtained for the ratio of the yield of Pa^{232} to that of Pa^{233} . It is of interest to note that the corresponding ratio of yields in the bombardment of uranium (thick target) with 60-in. cyclotron deuterons,¹ i.e., the ratio of the yield of 2.0-day Np^{238} to that of 2.3-day Np^{239} , is about 0.1. The errors in these values for the ratio of the yield of Pa^{232} to that of Pa^{233} and the ratio of the yield of Np^{238} to that of Np^{239} are such that these ratios might well be about equal.

Following are the approximate yields per 1000 $\mu\text{a-hr}$ of deuterons in the 60-in. cyclotron on a pure thick thorium target: about 10 millicuries of 1.6-day Pa^{232} plus, from the decay of this, about 1 microcurie of 30-year U^{232} ; and about 2 millicuries of 27.4-day Pa^{233} plus, from the decay of this, about 0.001 microcurie of 120,000-year U^{233} . For purposes of comparison, it may be stated that the bombardment² of 5 kg of thorium nitrate with the neutrons from 1000 $\mu\text{a-hr}$ of deuterons on beryllium in the 60-in. cyclotron produces about 10 millicuries of 27.4-day Pa^{233} and, from the decay of this, about 0.01 microcurie (0.5 μg) of 120,000-year U^{233} .

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Paper 2.6

NEUTRON ABSORPTION AND PRODUCTION BY U^{233}

By H. L. Anderson and A. N. May

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ABSTRACT

The total cross section of U^{233} was obtained from a transmission measurement on a 35-mg sample of U_3O_8 in which 87.4 per cent of the uranium was reported to be U^{233} . In one case the area of the sample was only 0.05 cm^2 . The total cross section reduced to a kT velocity of 2200 m/sec was found to be

$$\sigma(\text{total})U^{233} = 620 \pm 20 \text{ barns}$$

The error is largely due to the uncertainty in the isotopic purity.

The neutron emission per fission was found to be greater in U^{233} than in U^{235} by a factor 1.079 ± 0.02 . The neutron emission per thermal neutron absorbed was even greater, the factor being 1.13 ± 0.03 . The neutron emission was observed with cadmium-covered indium foils in the thermal column of CP-3, the Argonne low-power heavy-water-uranium reactor.

A comparison of the fission cross sections of U^{233} and U^{235} for thermal neutrons gave the ratio

$$\frac{\sigma(\text{fiss})U^{233}}{\sigma(\text{fiss})U^{235}} = 1.004 \pm 0.030$$

The values of the thermal-neutron constants for U^{233} compared with those of U^{235} are

	U ²³⁵	U ²³³
$\sigma(a)$	640 ± 13	620 ± 20
$\sigma(\text{fiss})$	548 ± 10	550 ± 20
$\sigma(c)$	92 ± 17	62 ± 28
ν	2.41 ± 0.10	2.60 ± 0.13
α	0.17 ± 0.03	0.11 ± 0.05

1. INTRODUCTION

The isotope U²³³ may be formed by neutron bombardment of thorium by the reactions

For the experiments reported here some 29 mg of the isotope, which had been extracted from slugs of thorium "carbonate" after an irradiation for about seven months in the Clinton pile, was available. The extractions of uranium from the thorium were carried out partly by B. L. Goldschmidt and his group at Montreal and partly by Hagemann, Studier, and Katzin at Chicago.¹ The two samples were mixed and finally purified by Katzin's group, who also supplied the following data on the specific activity of this sample:

Foil	Weight, μg	Specific activity of U element, dis/min/ μg
1	665	20,890
2	753	20,370

The average of these measurements is 20,630 alpha dis/min/ μg of uranium element. The specific activity of the pure isotope is given by Katzin¹ as 23,300 dis/min/ μg . This value is based on an earlier sample whose isotopic purity (85 per cent) was measured by A. J. Dempster, using the mass spectrograph, and whose specific activity was determined by counting the alpha particles in a low-geometry chamber from foils containing amounts of uranium determined by two separate methods. In one the total uranium in a solution was determined spectrophotometrically and an aliquot was evaporated onto a foil; in the other a part of a solution was evaporated upon a weighed platinum foil, ignited to U₃O₈, and weighed. The isotopic purity of our

sample, obtained by comparing its specific activity with that of the pure isotope, is 87.4 per cent. There is a doubt that this purity might be lower by 5 per cent. A direct mass-spectroscopic determination of this purity has been made by Rall and Dempster.²

2. DETERMINATION OF THE TOTAL CROSS SECTION

The total cross section for thermal neutrons was measured in transmission experiments on the thermal beam of the CP-2 pile, the Argonne low-power graphite-uranium reactor. The cross section was expected to be about 600 barns, leading to a thickness of about 0.5 g/cm^2 of the oxide for half transmission. Since only 40 mg of the U_3O_8 was available, it was clear that a very narrow beam, of the order of 0.1 cm^2 in area, would have to be used. To hold the material a brass cell was made consisting of two disks with an axial hole approximately $\frac{1}{8}$ in. in diameter [Fig. 1(a)]. An aluminum foil between the two disks formed the floor of the cell. The thermal-neutron beam was defined by two cadmium disks, with slightly smaller axial holes $\frac{3}{32}$ in. in diameter, which fitted above and below the cell. The diameter of the cell hole was determined accurately as 3.188 mm by measuring the diameter of a closely fitting steel plug. The whole unit was placed in the thermal-beam apparatus on the graphite pile, and the transmitted intensity was measured with a BF_3 counter (Fig. 2). A nearly identical brass cell was used with the same cadmium disks to give the intensity of the beam without absorber.

The oxide powder was transferred to the cell with a small platinum spatula and tamped down with a closely fitting steel rod. The top of the cell was then covered with Scotch tape to prevent accidental escape of the powder. The amount of oxide in the cell was determined by weighing before and after transfer and again after emptying the cell. Some variation of the weight of the full cell was observed, the extreme variation being 0.6 mg. This was ascribed to absorption of water vapor by the oxide and by the Scotch tape. The best weight was considered to be that given by the difference between the combined weight of the cell and oxide after drying and the weight of the cell after emptying. This gives 37.65 mg of U_3O_8 as the oxide content of the cell.

The pile was run at 20 kw, giving a counting rate of roughly 2000 c/min with the empty cell and 1000 c/min with the full cell. Counts were also taken with a cadmium sheet in the beam to give the background, which was mostly due to neutrons not coming through the cell hole. To test the identity of the two cells, runs were made in the same way after the oxide had been removed from its cell. From the figures in Table 1 the transmission corrected for the slight difference of the empty cells is

$$T = \frac{1100 - 41}{1970 - 41} \times \frac{2006 - 41}{1970 - 41} = \frac{1059}{1929} \times \frac{1965}{1929} = 0.5592$$

$$\ln \frac{1}{T} = 0.5812$$

Since the diameter of the cell is 3.188 mm, it has an area of 0.07982 cm². Dividing the U₃O₈ content of the cell, 37.65 mg, by the area gives 0.4717 g/cm². Taking a factor of 0.845 to go from U₃O₈ to U and a purity of 87.4 per cent U²³³, the result is

$$\frac{0.874 \times 0.4717 \times 0.845 \times 0.6023 \times 10^{24}}{233} = 9.005 \times 10^{20} \text{ atoms/cm}^2 \text{ of U}^{233}$$

Similarly there are 1.270×10^{20} atoms/cm² of ordinary uranium and 27.40×10^{20} atoms/cm² of oxygen.

To obtain the value of the total cross section reduced to a kT velocity of 2200 m/sec, the absorption part of the cross section must be corrected for the hardening of the thermal distribution and for the fact that the kT velocity of the beam is actually 2156 m/sec. The final value of the total cross section of U²³³ is obtained after subtracting the effect of the ordinary uranium and the oxygen. Assuming scattering cross sections of 8.3 barns for the uranium nuclei and 4.12 barns for the oxygen, we obtain a total scattering correction of 0.0198, which has to be subtracted from $\ln 1/T$, giving a corrected value of 0.5614. This now has to be corrected for the hardening of the thermal distribution, which gives a factor 0.9825, and for the effective velocity of the neutrons in the thermal beam, which has been determined as 2156 m/sec by the method of measuring the absorption in pyrex plates that have been calibrated on a velocity selector.³ These two corrections give $\ln 1/T = 0.5405$ for 2200 m/sec. This still has to be corrected for the absorption in ordinary uranium, for which the cross section is 7 barns, giving a correction of 0.0009. The corrected value of the transmission, replacing the term 0.0075 subtracted for scattering by U²³³, is

$$\ln \frac{1}{T} = 0.5396 + 0.0075 = 0.5471$$

leading to a total cross section for the isotope U²³³ of

$$\sigma(T) = 607.6 \text{ barns}$$

at a kT velocity of 2200 m/sec.

The principal sources of error in this experiment were the variations in weight and the uncertainty in lining up the two holes in the cadmium disks. The experiment was repeated using a similar cell made of beryllium which was light enough to be weighed on a microbalance [Fig. 1(b)]. A cover of aluminum foil, kept in place by a steel spring, was used in place of the Scotch tape. The two cadmium disks were kept in line by an outer brass holder. The lining up of the unit, and especially the fact that the whole neutron beam would clear the wall of the cell hole, was verified visually and by passing test rods. The diameter of the cell hole as measured by a closely fitting steel plug was 0.0992 in. The diameter of the hole in the cadmium disks was only slightly smaller, 0.0942 in. A nearly identical brass cell was made up to give the intensity without absorber.

The beryllium cell was filled and weighed after prolonged drying. The difference between this and the empty weight was taken as the content of the cell. The variation in weight while drying was of the same order (0.4 mg) as in the previous case. Runs were made in the same way as in the previous experiment. A fission chamber coated with enriched uranium and inserted in another part of the pile was used as a monitor. The variations in the monitor never exceeded 0.5 per cent.

In this case the empty cells are taken to be identical. The transmission (see Table 2) is therefore

$$T = \frac{1037}{2346} = 0.4420 \qquad \ln \frac{1}{T} = 0.8164$$

The diameter of the cell is 0.2520 cm, giving an area of 0.04988 cm². Dividing 33.47 mg by the area, we get 0.6710 g/cm² as the thickness. This leads to

$$\begin{aligned} U^{233} &= 12.810 \times 10^{20} \text{ atoms/cm}^2 \\ \text{Ordinary U} &= 1.831 \times 10^{20} \text{ atoms/cm}^2 \\ O &= 39.04 \times 10^{20} \text{ atoms/cm}^2 \end{aligned}$$

This gives a scattering correction of 0.0282, making $\ln 1/T = 0.7882$. The hardening correction is 1.0124, and the correction for the effective velocity is the same as above. The absorption in the ordinary uranium contributes 0.0013. After adding 0.0106 to restore the scattering by U^{233} , we get a final value of $\ln 1/T = 0.7914$, which with $12.81 \times 10^{20} \text{ atoms/cm}^2$ gives a total cross section of 617.7 barns for U^{233} . The difference between this and the previous value is not significant.

Both these measurements are subject to error from the grain size of the powder used. A sample was examined with a measuring microscope. The most frequent grain diameter was found to be about 0.02 mm, which would lead to a correction of about 0.5 per cent.

The deviations of the individual counts from their means are of the order of 1 per cent in both the above measurements, which is to be expected from the number of counts. The transmission ratio should have a statistical error of 1.2 per cent in the first experiment and 0.6 per cent in the second. The per cent error in $\ln 1/T$ is about twice this. The diameters of the cells were measured to 10^{-4} in. or 0.1 per cent, giving 0.2 per cent error in the area. The weight of the material was known to about 1 per cent in the first experiment and 0.3 per cent in the second. On this basis a weight of 1 has been assigned to the first experiment and a weight of 8 to the second experiment; therefore from the above causes the result is in error by 0.8 per cent. There is, in addition, an uncertainty of about 0.5 per cent in the grain-size correction and of 1 per cent in the kT velocity of the neutron beam. The result is, of course, subject to an uncertainty arising from the determination of the purity of the sample. A mass-spectrographic determination of the purity has been carried out by Rall and Dempster.² Our estimate of the purity is based on the ratio of two specific activity determinations, together with a mass-spectrographic measurement of the purity of another sample, so that the uncertainty in the knowledge of the purity amounts to about 3 per cent. This constitutes the largest uncertainty in our result.

The final result for the total cross section of U^{233} , reduced to a kT velocity of 2200 m/sec, is 620 ± 20 barns.

3. NUMBER OF NEUTRONS PER FISSION

The neutron emission of the sample of U^{233} was compared with that of an equal sample of U^{235} by placing first one and then the other sample at a suitable position inside the thermal column of CP-3 and observing the neutron emission with cadmium-covered indium foils placed at various distances from the sample. To minimize self-absorption in the samples, each was dissolved in heavy nitric acid and placed inside a quartz cell. The comparison of the number of fissions taking place in the two cells was made by removing an aliquot from each of the two solutions with a micropipet and evaporating this upon a platinum foil, making use of tetraethylene glycol to form a thin layer. Several foils prepared in this way were compared by fission counting inside the thermal column of CP-2. The ratio of the number of neutrons emitted per fission which is obtained in this way is given by

$$\frac{\nu(233)}{\nu(235)} = \frac{Q(233)}{Q(235)} \times \frac{F(235)}{F(233)} \times \frac{V(235)}{V(233)}$$

where Q is the integral of the cadmium-covered indium activity, F is the fission activity, and V is the volume of solution in the quartz cell. This determination is independent of the half life of U^{233} and of the isotopic purity of the samples.

The sample of U^{233} oxide was dissolved in heavy nitric acid which had been prepared by passing NO_2 gas through heavy water. A mass-spectroscopic analysis showed that the acid contained only 0.3 per cent of light hydrogen so that the scattering mean free path within the solution was only slightly smaller than in the surrounding graphite. Unfortunately, the heavy nitric acid was found to contain hydrochloric acid as well. This dissolved some 18 mg of platinum from the crucible in which the U^{233} oxide had been prepared. The presence of this amount of platinum did not affect the determination of ν , since its contribution to the self-absorption of the sample was negligible. Its introduction, however, made it impossible to secure an independent check on the specific alpha activity of the sample.

The sample of U^{235} oxide which was available did not have as high an isotopic purity as the sample of U^{233} . The enriched material designated E10A was used, for which the ratio of isotope U^{238} to isotope U^{235} is known to be 8.05 from a number of independent determinations made by E. Fermi. The same heavy nitric acid which served for the U^{233} sample was used to dissolve 273.7 mg of E10A oxide (25.35 mg of U^{235} isotope). The contents of the U^{233} cell as determined by alpha counting an aliquot in a low-geometry alpha chamber and by using 23,300 dis/min/ μg as the specific activity of the pure isotope was 27.12 mg of U^{233} isotope. After the removal of the aliquots the volumes of the solutions as they were used in the comparison of the neutron emission were

Cell	Volume, μl	Amount of isotope, mg
235	4974	25.20
233	5174	26.38

With such small amounts of material, the self-absorption effect in the cells is quite small; the difference in the self-absorption effect between the two cells is certainly negligible.

4. COMPARISON OF THE NEUTRON EMISSION

The comparison of the neutron emission from the two cells was made by irradiating them in the thermal column of CP-3 and observing their neutron emission with cadmium-covered indium foils. Some care had to be taken in the choice of the position of the cells inside the thermal column, so that the background of primary fast neutrons would not be excessive. Guided by the survey made by L. Seren (as reported by E. Fermi⁴), the cell position was chosen at 105 cm from the front face of the thermal column (an additional 2 ft of graphite reflector separates the front face of the thermal column from the reactor tank). This left 135 cm to the outside face of the thermal column. Since the column has a 152-cm side, measurements of indium resonance neutrons made along the axis differ inappreciably from those which would be obtained in an infinite graphite column. As Tables 3 and 4 will show, the measured intensity was more than equal to the background even at 52.4 cm from the cell.

All the measurements were made using the standard indium foils (0.0924 g/cm^2 and $6.5 \text{ by } 4 \text{ cm}^2$), which during the irradiation were mounted inside a cylindrical cadmium holder which provided at least 1.73 g/cm^2 of cadmium protection in any direction.

The measurements were limited to three positions, 22, 37.3, and 52.4 cm from the cell. Since it was difficult to reproduce the irradiations exactly, a small indium monitor foil (21.5 mg) unprotected by cadmium was mounted near the cell as a measure of the thermal-neutron exposure. The beta activity of the standard indium foils was measured after the end of the irradiation twice on each of three counters according to a definite time schedule, in order to minimize errors due to uncertainties in the lifetime of indium. The monitor foil was measured by observing its gamma-ray activity with a Lauritsen electroscope. The irradiations were made at a power of 60 kw for 30 min. Each figure in columns 2, 5, and 8 of Table 3 is the mean of the activity obtained from the three counting sets, corrected for decay. Columns 3, 6, and 9 give the correcting factor deduced from the monitor activities, normalized to unity for the first monitor, while columns 4, 7, and 10 give the activities corrected by the monitor factor. The mean square deviation of the readings in columns 4, 7, and 10 from their means is 1.5 per cent. The means of the three foil readings at each distance should therefore have a mean square error of about 1 per cent. Table 4 gives the activities at each distance with the background subtracted and the ratio of the effects due to the U^{233} and U^{235} samples. These ratios will have a mean square error of 1.4

per cent, so that their differences are not significant. From this it follows that the age of U^{233} fission neutrons is the same as that of U^{235} to within 2 per cent.

In taking the means of the ratios they were weighted with the intensity, with the square of the distance from the cell, and with factors 3, 2.5, and 2 at 22, 37.3, and 52.4 cm, respectively. The latter factors take account of the reduction of the accuracy of the distant points by the background. The counts due to the U^{233} and U^{235} cells and to the background are plotted in Fig. 3. The smooth curves are based on the experiments of Fermi, Marshall, and Marshall⁵ and on Seren's figures. We adopt 1.144 ± 0.010 as the weighted mean of the ratio $Q(233)/Q(235)$.

5. COMPARISON OF FISSION RATE

The ratio of the number of fissions per second in the two cells was determined by counting the number of fission pulses produced in an ionization chamber in the thermal column of the CP-2 pile when foils prepared from aliquot parts of the cell solutions were placed in it. Two foils, K8 and K9, were prepared, using for each 31.35 μ l of the U^{235} solution; and two foils were made from the U^{233} solution, one D5 with 31.35 μ l and the other J1 with 54.9 μ l. The thickness of the uranium oxide layers was kept around 50 μ g/cm² by using a larger foil for the U^{235} samples. The active area of the U^{235} layers was about 40 cm², that of the U^{233} layers about 5 cm². These foils were mounted in turn on the (negative) high-tension electrode of a parallel-plate chamber which was filled with hydrogen gas to 1 atm. The chamber was inserted in a hole in the thermal column so that it was in a nearly uniform neutron field. The pile was run at 0.5 kw and monitored as before with the enriched fission chamber. Again the variations did not exceed 1/2 per cent.

A perfectly thin foil should give a plateau over which the number of fissions counted is independent of the gain setting of the amplifier. To test this, counts were made at a number of different gains. Table 5 and Fig. 4 give the counts per minute corrected for the background (4 c/min, caused by slight contamination of the chamber) observed when there was no foil present. The count due to coincident alpha pulses was negligible for all the gain settings actually used.

The first column gives in arbitrary units the minimum input-pulse size counted at the gain setting used. In these units the maximum pulse size was 28.6. The figures in the column headed "J1 corr." have been multiplied by 31.35/54.9 to bring the counts on this foil to the same volume of solution as the others. The figures in the last

row give the mean slope of the plateau in terms of the change in count when the minimum counted pulse size is changed by one-quarter of the maximum, i.e., by 7 arbitrary units. This figure is estimated to give the fraction of fission counts lost by complete absorption in the deposit. It is considerably greater than would be expected from the mean thickness of the deposits, indicating that they are not uniform.

These results can be reduced in two ways. In the first, each plateau is extrapolated to zero pulse size, and the losses in the deposit are corrected for by the slope factors in the last row of Table 5. This gives the figures in the "Adjusted" row of Table 5 and a ratio 1.013 between the specific fission rates of the U^{233} and U^{235} solutions. Alternatively, we may take the ratios of the U^{233} and U^{235} foils at each gain setting, which are given in the last column of Table 5, and have a mean value 1.025. The effect of the absorption in the deposits is reduced in this method because only the difference in the slopes of the U^{233} and U^{235} plateaus is important. We adopt as the mean figure 1.019. This will have an error of about 1.4 per cent, most of which arises from the effect of the thickness of the deposits.

It is now possible to calculate the ratio of the neutron emission per fission from U^{233} and U^{235} .

$$\frac{U^{233}}{U^{235}} = 1.144 \times \frac{4974}{5174} \times \frac{1}{1.019} = 1.079 \pm 0.02$$

This result is independent of uncertainties in the purity of the samples and of the half life of U^{233} . If we assume $\nu(235) = 2.41$, we obtain $\nu(233) = 2.60$.

6. FISSION CROSS SECTION AND VALUE OF η

The ratio of the fission cross sections may be obtained from the above data, together with a knowledge of the amounts of U^{233} and U^{235} on each foil. The amount of U^{235} is known from the weight of oxide put in the cell. The amount of the U^{233} was obtained from an alpha count of the foils based on the specific activity, 23,300 dis/min/ μ g, given by L. I. Katzin. We are indebted to H. Heskett for the measurements of the alpha activity of the foils. He used a low-geometry arrangement in which the fraction of the alphas counted was 1/6083. The results of his measurements are listed in Table 6; a typical plateau curve is shown in Fig. 5.

In the preceding section the ratio 1.025 was found for the fission activity foils of U^{233} and U^{235} reduced to the same volume of solution. The concentration of isotope U^{235} was 5.066 g per liter; thus

$$\frac{\sigma(\text{fiss})\text{U}^{233}}{\sigma(\text{fiss})\text{U}^{235}} = 1.019 \times \frac{5.066}{5.100} \times \frac{233}{235} = 1.004$$

The uncertainty in the specific activity of U^{233} is about 2 per cent. An error of 1.4 per cent has already been assigned to the fission comparison. The isotopic purity of the U^{235} sample is uncertain by 1 per cent, while the alpha counting of the U^{233} foils is subject to an error of about 1 per cent. The fission cross section of U^{233} , therefore, is 1.004 times that of U^{235} with an accuracy of 3 per cent.

According to measurements reported by Bailey, Blair, and Russell⁶ and also those carried out by L. Marshall at Argonne, the fission cross section of U^{235} reduced to a kT velocity of 2200 m/sec is 548 ± 10 barns. The difference between the absorption and fission cross sections of U^{233} is ascribed to radiative capture.

$$\sigma(c)\text{U}^{233} = 62 \pm 28 \text{ barns}$$

The absorption cross section was obtained by subtracting 8 barns, which was due to scattering, from the total cross section.

The ratio of capture to fission cross sections has the value

$$\alpha(233) = 0.11 \pm 0.05$$

The important constant from the point of view of pile design is η , the number of neutrons produced per thermal neutron absorbed. Compared to U^{235} the present measurements give

$$\begin{aligned} \frac{\eta(233)}{\eta(235)} &= 1.144 \times \frac{25.20}{26.38} \times \frac{233}{235} \times \frac{640}{612} \\ &= 1.133 \pm 0.03 \end{aligned}$$

Table 1 — First Transmission Experiment on U^{233}
(Values given in counts per minute)

Blank cell, 5-min runs	U^{233} cell, 10-min runs	Cadmium, 5-min runs	After emptying U^{233} cell	
			Blank cell, 5-min runs	Empty U^{233} cell, 5-min runs
1990	1106	41	2016	1966
1972	1106	42	1996	1975
1975	1086	40		
1948	1090			
1965	1112			
Av. 1970	1100	41	2006	1970

Table 2 — Second Transmission Experiment on U^{233}
(Values given in counts per minute)

Blank cell, 5-min runs	U^{233} cell, 10-min runs	Cadmium, 5-min runs	After emptying U^{233} cell	
			Blank cell, 5-min runs	Empty U^{233} cell, 5-min runs
2355	1080	39	2359	2454
2348	1057	31	2429	2419
2363	1085	40	2448	2418
2372	1071	39	2424	2399
2404	1073			
2410	1079			
2408				
2402				
Av. 2383	1074	37	2415	2422

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Table 3

Distance, cm	U ²³⁵ cell			U ²³⁵ cell			Blank		
	Activity, c/min	Monitor factor	Corr. activity, c/min	Activity, c/min	Monitor factor	Corr. activity, c/min	Activity, c/min	Monitor factor	Corr. activity, c/min
22.0	19712	1.000	19712	17442	1.017	17739	5140	0.962	4945
	19727	1.004	19806	17024	1.082	18420	4765	1.111	5294
	18308	1.127	20633	16918	1.114	18847			
			Av. 20050			Av. 18335			Av. 5119
37.3	8962	1.000	8962	7941	1.017	8076	2679	0.962	2577
	8983	1.004	9019	7583	1.082	8205	2503	1.111	2781
	8089	1.127	9116	7514	1.114	8371			
			Av. 9032			Av. 8217			Av. 2679
52.4	3436	1.000	3436	3052	1.017	3104	1413	0.962	1359
	3358	1.004	3371	2902	1.082	3140	1283	1.111	1425
	3057	1.127	3445	2890	1.114	3219			
			Av. 3417			Av. 3154			Av. 1392

Table 4

Distance, cm	Activity, c/min		
	Blank U ²³³ cell	Blank U ²³⁵ cell	U ²³³ /U ²³⁵ ratio
22	14931	13216	1.1298
37.3	6353	5538	1.1472
52.4	2025	1762	1.1493
Weighted mean			1.144

Table 5

Pulse size, arbitrary units	Activity, c/min							U ²³³ /U ²³⁵ ratio
	D5	J1	J1 corr.	K8	K9	U ²³³ mean	U ²³⁵ mean	
3.2		10300	5881	5835		5881	5835	1.008
5.2	6131	10261	5859	5857	5714	5995	5785	1.036
8.2	6035	10178	5812		5829	5923	5829	1.016
11.1	6089	10014	5718	5651	5766	5903	5708	1.034
14.1	6029	9781	5585	5612		5807	5612	1.035
16.7	5720	8984	5130	5302		5426	5302	1.023
								Av. 1.025
Adjusted	6137	10540	6018			6077	6000	1.013
Mean slope, %	0.5	1.6		1.9				

Table 6

Foil	Vol. of pipet, μl	Alpha dis/min	U ²³³ , g per liter
J1	54.9	6.442×10^6	5.036
D1	34.6	4.130×10^6	5.123
J6	54.9	6.466×10^6	5.055
D5	31.35	3.787×10^6	5.187
			Av. 5.100

Fig. 1—Cells for transmission experiments.

Fig. 2— BF_3 chamber geometry used in transmission measurements.

Fig. 3—Activation of Cd-covered indium detectors due to cells containing U^{233} and U^{235} placed in CP-3 thermal column. Smooth curves are fitted from the data of Fermi, Marshall, and Marshall (Report CP-1084) and Seren.

Fig. 4—Plateaus of fission counts.

Fig. 5—Typical alpha-counting plateau (foil J5).

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Paper 2.7

ETA FOR U^{233}

By Walter H. Zinn and Herbert Kanner

[Editor's Note: This paper is a contribution from the Metallurgical Laboratory, University of Chicago. Based on Report CF-3651. The work reported herein was carried out in the period March to July 1945. Physical measurements were made by H. V. Lichtenberger, W. H. Zinn, R. Nobles, G. S. Monk, A. S. Langsdorf, Jr., R. Purbriek, H. Kubitschek, and S. M. Dancoff. The chemical preparation of the materials was done by L. I. Katzin, M. H. Studier, E. K. Hyde, F. Hagemann, and N. N. Hellman.]

ABSTRACT

Measurements of η and σ_a for U^{233} and U^{235} and $\sigma_{fiss}(U^{233})/\sigma_{fiss}(U^{235})$ have been made. These lead to the following set of constants for U^{233} :

$$\left. \begin{array}{l} \nu = 2.61 \\ \eta = 2.34 \pm 0.06 \\ \alpha = 0.114 \\ \sigma_a = 566 \pm 15 \text{ barns} \\ \sigma_{fiss} = 508 \pm 20 \text{ barns} \\ \sigma_c = 58 \text{ barns} \end{array} \right\} 2200 \text{ m/sec}$$

[The values for η and σ_a represent conservative estimates of the probable errors.]

1. INTRODUCTION

The following measurements were made for the purpose of obtaining a consistent set of constants for U^{233} :

1. Direct determination of $\sigma_a(U^{233})$ and $\sigma_a(U^{235})$ by transmission measurements.

2. Direct determination of $\eta(U^{233})$ and $\eta(U^{235})$ by danger coefficients measured by the "swing" method.
3. Determination of $\eta(U^{233})/\eta(U^{235})$ by counting the fast neutrons emitted by samples placed in a thermal beam.
4. Determination of $\sigma_{fiss}(U^{233})/\sigma_{fiss}(U^{235})$ by fission counting.

2. THEORY OF THE EXPERIMENTS

2.1 σ_a by Transmission. The transmission for monoenergetic neutrons of a sample of U^{233} or U^{235} (containing some U^{238}) in the form U_3O_8 is given by

$$-\ln T = N_{U^{233}}\sigma_a(U^{233}) + N_{U^{238}}\sigma_a(U^{238}) + \Sigma N\sigma_s \quad (1)$$

where T = transmission

N = atoms per square centimeter

$$\Sigma N\sigma_s = N_{U^{233}}\sigma_s(U^{233}) + N_{U^{238}}\sigma_s(U^{238}) + N_O\sigma_s(O)$$

A correction has to be made to Eq. 1 if the neutron beam is not monoenergetic to allow for the hardening of the beam as it passes through the sample. If the distribution of neutron velocities is Maxwellian, as it is from a thermal column, and the absorber and detector follow a $1/v$ law, the so-called "Bethe correction" will allow for this hardening. (Subsequent experiments have shown that σ_a for both U^{233} and U^{235} is approximately proportional to $1/v$ in the thermal region.) The factor used, β , is a function of the numerical value of $-\ln T - N\sigma_s$; $\beta(-\ln T - \Sigma N\sigma_s)$ is the $-\ln T - \Sigma N\sigma_s$ that would be observed were the measurement made with a monochromatic beam of kT neutrons. The scattering terms are subtracted from $-\ln T$ before the application of β , since the scattering cross section is assumed to be energy-independent. Equation 1 can then be replaced by

$$[N_{U^{233}}\sigma_a(U^{233})]kT + [N_{U^{238}}\sigma_a(U^{238})]kT = \beta[-\ln T - \Sigma N\sigma_s] \quad (2)$$

The following values⁵ for cross sections have been accepted:

$$\sigma_a(U^{238}) = 2.6 \text{ barns}$$

$$\sigma_s(U^{233}) = \sigma_s(U^{235}) = 8.5 \text{ barns (assumed)}$$

$$\sigma_s(O) = 4.0 \text{ barns}$$

2.2 η by Swings. Measurement of danger coefficients by the swing method consists in oscillating the sample in and out of the pile with the control rods in a fixed position, all oscillations occupying the

same time interval. The pile should be very closely critical. Under these conditions, the galvanometer deflections S will be proportional to the change in i_h caused by the insertion of the sample.

For a fissionable material, for example U^{233} , the deflections are expressed by

$$S_{U^{233}} \approx \Delta i_{h_{U^{233}}} \approx nv N_{U^{233}} \sigma_a(U^{233}) [\eta(U^{233}) C - 1] R \quad (3)$$

where R is the resonance correction. For a nonfissionable material such as boron ($\eta = 0$), they are expressed by

$$S_B \approx \Delta i_{h_B} \approx nv N_B \sigma_a(B) (-1)R \quad (4)$$

In Eqs. 3 and 4, N is the total number of atoms in the sample, and C is the product of the following three factors:

1. Probability of 0.87 that fast neutrons from U^{233} escape resonance capture in uranium lumps during the slowing-down process. This is the accepted value of p for the CP-2 pile.

2. A factor allowing for the fact that some of the neutrons from U^{233} diffuse to regions of lower statistical weight and have less effect on the pile reactivity. This factor is 0.969 and was calculated.

3. A factor of increase allowing for the production of additional neutrons from the U^{233} neutrons by fast effect. The normal fast effect in a pile is about 4 per cent.

The fast effect is due mainly to fast fission produced by neutrons before they leave the lumps in which they were formed, as the probability is very low that a neutron will enter the moderator and still have enough energy to produce fast fission when it next encounters a lump. In the swing measurement, the sample has small dimensions compared to a pile lump, and the probability of fast fission in the sample is correspondingly lower. The fast effect ϵ has in this case been estimated to be 1 per cent, giving a factor of $1 + \epsilon$, or 1.01.

Therefore

$$C = (0.87) (0.969) (1.01) = 0.851$$

The resonance correction, a factor allowing for the capture of neutrons by the sample before they have been slowed down to thermal energy, is the ratio of the total number of neutrons captured to the number of thermal neutrons captured. The value of this correction was obtained experimentally for boron and inferred for U^{233} and U^{235} from a comparison of their cross sections for fast neutrons to that of

boron. A set of values calculated by Dancoff from data obtained by Fermi and Anderson¹ are

Element	Resonance correction
Boron	1.026
U^{233}	1.090
U^{235}	1.034

During the swing measurements nv is kept constant, and numbers proportional to $N\sigma_a$ are obtained from the previously considered transmission measurements. Equations 3 and 4 can then be solved for η .

2.3 $\eta(U^{233})/\eta(U^{235})$ by Long-counter Data. The ratio $\eta(U^{233})/\eta(U^{235})$ can be determined by successively placing samples of U^{233} and U^{235} in a collimated thermal beam and counting the fission neutrons with a "long" counter (a counter with energy-independent response). Since the samples will also scatter neutrons into the counter, the counts obtained from a similar sample of depleted U^{238} have to be subtracted from the U^{233} and U^{235} counts, the difference being the true fast-neutron count. Then

$$\frac{c/\min(U^{233} - U^{238})}{c/\min(U^{235} - U^{238})} = \frac{nv [1 - T(U^{233})] \eta(U^{233})G}{nv [1 - T(U^{235})] \eta(U^{235})G} \quad (5)$$

where T is the transmission of the sample as measured, using the same geometry with respect to the beam, and G is a geometry factor for the long counter. The terms nv and G can be kept constant and may therefore be canceled from the expression.

Errors due to slight differences in geometry between the transmission and long-counter measurements may be minimized by designing the samples to have similar transmissions.

3. EXPERIMENTS

3.1 σ_a by Transmission Measurements. Five hardened-steel cells to contain the powdered samples were constructed in the course of this work (Fig. 1a). They were designed for maximum accuracy in knowledge of the mass per unit area of the contents and in reproducibility of the position and size of the apertures. Great pains were taken to make sure that the powder cavities of the cells were perfectly cylindrical. They were carefully lapped and both ends of each one measured along many different diameters with a traveling microscope. Then the weighed cells were loaded with U^{233} or U^{235} in the form U_3O_8 and the contents firmly pressed by the use of plungers (Fig. 1b). Identical unloaded cells were used for the "open" measurements. The

uniformity of distribution of powder in the cells was checked by measuring their transmissions with a beam collimated by pinholes. The entire surface of the cell apertures was so measured, and the transmissions were observed to be constant. Table 1 gives a complete listing of the cell contents and areas.

Several different mounting arrangements were used as the measurements progressed in order to improve the reproducibility of the geometry. In measurements 1 to 5, a sliding mount was used to allow a rapid and accurate interchange of the cells (Fig. 2). Suspicion that this mount might introduce a positioning error caused the substitution of a stationary cell mount for the slider in measurement 6 (Fig. 6). This was the same mount that was later used for the long-counter measurements. Each cell in turn was merely set on the pins, assuring perfect reproduction of position. Finally an "optical bench" was built (Fig. 3). This consisted of a long bar with an accurately machined V-shaped groove. The powder cells and cadmium collimators, having the same diameter and aperture as the cells, could be set along this bar. The optical bench geometry was used in measurements 7 and 8.

Table 2 contains the data and results of all the transmission experiments. As explained in Sec. 2, Eq. 2 gives σ_a/kT . In order to reduce this to σ_a for neutrons of velocity 2200 m/sec, it was necessary to measure the effective velocity of the thermal beam. This was done by measuring in the same beam the transmission of a pyrex or gold plate which had been previously calibrated by use of the mechanical velocity selector. The pyrex plate had been previously used for this purpose at Argonne.² The gold plate was also calibrated by means of the crystal spectrometer. The calibration curves for these plates gave transmission as a function of effective neutron velocity. Then the measured σ_a was corrected on the basis that $\sigma_a \approx 1/v$. The effect on the σ_a measurements of the grain size of the powder used was calculated and found to be negligible compared to the other uncertainties of the experiment.

For an example of the calculation procedure, consider measurement 7 on cell 4. According to Table 1, cell 4 contained 0.32512 g of U^{233} of 96.2 per cent enrichment in the form U_3O_8 . Then the U^{238} in the material was equal to 100 per cent minus 96.2 per cent, or 3.8 per cent.

To determine the grams of U^{233} , U^{238} , and oxygen in the sample:

$$\begin{array}{rcl} U^{233}: & 3 \times 0.962 \times 233 = & 672.4 \\ U^{238}: & 3 \times 0.038 \times 238 = & 27.1 \\ O: & 8 \times 16 = & 128.0 \\ \hline \text{Total} & & 827.5 \end{array}$$

$$U^{233} = \frac{672.4}{827.5} \times 0.32512 \text{ g} = 0.2642 \text{ g}$$

$$U^{238} = \frac{27.1}{827.5} \times 0.32512 \text{ g} = 0.01063 \text{ g}$$

$$O = \frac{128.0}{827.5} \times 0.32512 \text{ g} = 0.05030 \text{ g}$$

The atoms per square centimeter for each of these elements were then computed, using the above weights and the value for the area of the cell given in Table 1.

From Table 2, the transmission observed was 0.5321 with neutrons of effective velocity 2155 m/sec; $-\ln(0.5321) = 0.6309$. The part of this due to scattering was

$$N_{U^{233}}\sigma_s(U^{233}) + N_{U^{238}}\sigma_s(U^{238}) + N_O\sigma_s(O) = (10.14 \times 10^{20} \\ + 0.3996 \times 10^{20})(8.5 \times 10^{-24}) + (28.12 \times 10^{20})(4.0 \times 10^{-24}) = 0.0202$$

Therefore

$$-\ln T - \Sigma N\sigma_s = 0.6309 - 0.0202 = 0.6107$$

The Bethe hardening correction for $-\ln T = 0.6107$ is 0.988.

$$N_{U^{233}}\sigma_a(U^{233}) + N_{U^{238}}\sigma_a(U^{238}) = (0.988)(0.6107) = 0.6034$$

and

$$N_{U^{233}}\sigma_a(U^{238}) = (0.3996 \times 10^{20})(2.6 \times 10^{-24}) = 0.0001$$

and consequently

$$N_{U^{233}}\sigma_a(U^{233}) = 0.6034 - 0.0001 = 0.6033$$

or

$$\sigma_a(U^{233}) \left[2155 \text{ m/sec} \right] = \frac{0.6033}{10.14 \times 10^{20} \text{ cm}^{-2}} = 595 \text{ barns}$$

Applying $\sigma_a \approx 1/v$,

$$\sigma_a(U^{233}) \left[2200 \text{ m/sec} \right] = \frac{2155}{2200} \times 595 \text{ barns} = 583 \text{ barns}$$

3.2 η by Swing Measurements. The sample material was diluted with aluminum powder and distributed in five aluminum cans to re-

duce self-protection (Fig. 4). The only feasible method found for making sufficiently uniform sets of cans was die drawing. The contents of the four sets of cans used are listed in Table 3.

Graphite stringer 23T of CP-2 was used for this experiment. Figure 5a shows the position of the cans relative to the center of the pile and to the nearest lumps. In any given measurement, a set of sample cans was compared to the dummy set by alternately placing these sets near the center of the pile. This was done by having the two sets clipped to an aluminum strip which ran the length of the stringer and extended out of the pile at both ends. The two sets of cans were attached 8 ft apart. Dead stops were set up defining two positions of the strip at which the two sets would alternately be at the center of the pile. During a run the projecting end of the strip would be flung from one position to the other every 10 sec by two men standing 8 ft apart (Fig. 5b). When a set was at the center of the pile each can would be at the maximum possible distance from the nearest lump, thus minimizing the effect of any small error in positioning of the set. The observed swings were the galvanometer deflections caused by this 8-ft shift. Since by this arrangement each of the two sets would leave the center of the pile for points (on opposite sides of the center) which might have different statistical weights, a complete measurement required interchanging the two sets on the strip. The averages of the observed swings and one sample set of actual swings are recorded in Table 4.

As stated in Sec. 2, values of $N\sigma_a$ were needed for all the samples in addition to the values of Δih . For the U^{233} and U^{235} samples, these were obtained from the average values of $\sigma_a kT$ given in Table 2. For the pyrex sample a separate transmission determination had to be made. A number of small squares (about 1 cm²) were cut from a sheet of pyrex, their weight and area determined, and their transmissions measured with the same beam as was used for the cell transmissions. The rest of the pyrex sheet was ground to a fine powder for use in the swing measurement. (It was noted that, during grinding, the pyrex gained 2.066 per cent in weight from abrasion of the agate mortar.)

The pyrex square chosen as characteristic had a $-\ln T$ of 0.3947. Applying a Bethe factor of 0.9570 and a further factor of 0.950 to allow for the inclusion of scattering in $-\ln T$, the corrected $-\ln T$ was $(0.3947)(0.9570)(0.950) = 0.3588$. This plate weighed 0.7634 g and had an area of 3.524 cm², or 0.2166 g/cm². Since $-\ln T = \text{atoms/cm}^2 \times \sigma_a$, the value of $N\sigma_a$ (N is the total number of atoms) for 1 cm² gives 0.2166 g of the plate equal to 0.3588 cm².

There was 0.2720 g of pyrex powder in the cans (Table 3). $N\sigma_a$ for the pyrex powder then was

$$0.3588 \text{ cm}^2 \times \frac{0.2720 \text{ g}}{0.2166 \text{ g}} = 0.4506 \text{ cm}^2$$

From Table 2, the value $\sigma_a[kT]$ of U^{233} was $580.1 \times 10^{-24} \text{ cm}^2$. There were 8.254×10^{20} atoms of U^{233} in the U^{233} set of cans (Table 3). $N\sigma_a$ for this set was then

$$(8.254 \times 10^{20}) (580.1 \times 10^{-24} \text{ cm}^2) = 0.4788 \text{ cm}^2$$

Similarly, for the U^{235} set, $\sigma_a(U^{235})[kT]$ was $658.8 \times 10^{-24} \text{ cm}^2$, and there were 7.048×10^{20} atoms of U^{235} in the cans.

$$N\sigma_a = (7.048 \times 10^{20}) (658.8 \times 10^{-24} \text{ cm}^2) = 0.4643 \text{ cm}^2$$

To summarize:

Can contents	$N\sigma_a$ of contents, cm^2
Pyrex	0.4506
U^{233}	0.4788
U^{235}	0.4643

These values for $N\sigma_a$ and the values for Δih taken from Table 4 are now entered in Eqs. 3 and 4 (see Sec. 2), giving

$$\Delta ih(B) = -66.6 = K nv (0.4506) (-1) (1.026)$$

where K is a constant of proportionality, or $K nv = \frac{66.6}{(0.4506) (1.026)} = 144.0$.

$$\begin{aligned} \Delta ih(U^{233}) &= 73.7 = K nv (0.4788) [\eta(U^{233}) C - 1] (1.090) \\ &= (144.0) (0.4788) [\eta(U^{233}) \times 0.851 - 1] (1.090) \end{aligned}$$

or $\eta(U^{233}) = 2.33$. Similarly,

$$\Delta ih(U^{235}) = 55.0 = (144.0) (0.4643) [\eta(U^{235}) \times 0.851 - 1] (1.034)$$

or $\eta(U^{235}) = 2.11$.

3.3 Determination of $\eta(U^{233})/\eta(U^{235})$. Three powder cells were used for this measurement: cells 4 and 5 and a similar U^{238} cell containing 325.0 mg of depleted U_3O_8 . The transmissions of cells 4 and 5 were measured using the optical bench (measurements 7 and 8, Table

2). Then the counting rate on the long counter was observed for all three cells using the mounting arrangement shown in Fig. 6. It should be noted that all three cells contained about the same weight of U_3O_8 and were otherwise identical. Thus the scattering of thermal neutrons into the long counter should be the same for all three.

A sample set of data is given in Table 5, all total counts being for the same number of monitor counts.

Similar sets of data were taken with the counter at 20, 30, and 40 cm from the cell. Increasing this distance reduced the maximum obliquity at which neutrons could enter the counter. Since the flatness of response of a long counter varies somewhat with the entrance angle of the neutrons, this checked whether there was any dependence or distance due to differences in the fission spectra of U^{233} and U^{235} . Still another run was made after placing an additional 50 cm of graphite in the beam, raising the Cd ratio from 28×10^3 to 90×10^3 . This gave a check on whether there was any effect from the few fast neutrons in the thermal beam. Both of these variables produced no apparent effect. The summarized data are included in Table 6.

From Eq. 5,

$$\frac{\eta(U^{233})}{\eta(U^{235})} = \frac{U^{233}}{U^{235}} \frac{1 - T_{U^{235}}}{1 - T_{U^{233}}} = (1.147) \frac{1 - 0.5454}{1 - 0.5321} = 1.114$$

3.4 Determination of $\sigma_{fiss}(U^{233})/\sigma_{fiss}(U^{235})$. The ratio of the fission cross sections of U^{233} and U^{235} was determined by fission counting of thin foils. This experiment was performed three times using as many distinct sets of foils with slight differences in procedure.

Two properties of the measurements had to be established before the results could be considered valid: (1) The counting rate had to be independent of amplifier gain in the gain region used; (2) the counts per minute per atom of fissionable material had to be independent of foil thickness.

In the first determination only one fission chamber of a quick-opening type was used (Fig. 7). It was monitored by a standard BF_3 counter. Three foils each of U^{233} and U^{235} in the form U_3O_8 were used at four different amplifier gains. The results are shown in Table 7. It can be seen from the data that there was no systematic variation in c/m-A (fission counts per atom divided by monitor counts in arbitrary units) with either foil thickness or gain.

Two chambers were used simultaneously in the second and third determinations. The need for monitoring was circumvented by cycling the measurements as follows: While a U^{233} foil was being counted in the first chamber, a U^{235} foil was counted in the second; then the two foils were interchanged and the count repeated. The independence of

counting rate on gain setting was shown by the flatness of gain plateaus taken on the two chambers, and independence on foil thickness by the fact that a graph of micrograms of fissionable element on the foils against counting rate turned out to be a straight line passing through the origin (Figs. 8 and 9).

The foils used in the second set of measurements are listed in Table 8.

In this run a complete cycle of measurements consisted of the two counts mentioned above, followed by a repetition after interchanging the two chambers in position. The summarized data and ratios are given in Table 9.

Concern as to the accuracy of the values of the weights of the foils led to the plating of a new set of foils at Argonne.

The values for these were

U^{233} set		U^{235} set	
Foil No.	μg of element	Foil No.	μg of element
5	12.00	5	20.86
6	24.00	6	41.72

The third set of data was obtained from these, with the unnecessary interchanging of chamber positions omitted.

The summarized results were as shown in Table 10.

4. SUMMARY

The direct experimental results were

$\sigma_a(U^{233}) = 566 \text{ barns}$	}	Transmission experiment
$\sigma_a(U^{235}) = 642 \text{ barns}$		
$\eta(U^{233}) = 2.33$	}	Swing measurement
$\eta(U^{235}) = 2.11$		
$\frac{\eta(U^{233})}{\eta(U^{235})} = 1.114$		Long-counter experiment
$\frac{\sigma_{fiss}(U^{233})}{\sigma_{fiss}(U^{235})} = \frac{0.9071}{0.953}$	} Av. = 0.928	Fission counting
0.9226		

Also, accepting the value of 2.11 for $\eta(U^{235})$ [value of $\eta(U^{235})$ calculated from values of ν and α for U^{235} given in Report LA-140A is 2.12]

$$\eta(U^{233}) = 2.11 \frac{\eta(U^{233})}{\eta(U^{235})} = 2.11 \times 1.114 = 2.35$$

An average value of 2.34 for $\eta(U^{233})$ may then be accepted.

By combining the above results with an assumed value of 548 barns for $\sigma_{\text{fiss}}(U^{233})$, values for ν , σ_{fiss} , and σ_c may be calculated for U^{233} by use of the relation $\eta = \nu/(1 + \alpha)$, where $\alpha = \sigma_c/\sigma_{\text{fiss}}$.

$$\sigma_{\text{fiss}}(U^{233}) = \sigma_{\text{fiss}}(U^{235}) \left[\frac{\sigma_{\text{fiss}}(U^{233})}{\sigma_{\text{fiss}}(U^{235})} \right] = (548) (0.928) = 508 \text{ barns}$$

$$\text{Since } \sigma_a = \sigma_c + \sigma_{\text{fiss}},$$

$$\sigma_c(U^{233}) = 566 - 508 = 58 \text{ barns}$$

$$\alpha(U^{233}) = \frac{58}{508} = 0.114$$

$$\nu(U^{233}) = \eta(1 + \alpha) = (2.34) (1.114) = 2.61$$

A complete list, then, of the constants of U^{233} is

$$\left. \begin{array}{l} \nu = 2.61 \\ \eta = 2.34 \pm 0.06 \\ \alpha = 0.114 \\ \sigma_a = 566 \pm 15 \text{ barns} \\ \sigma_{\text{fiss}} = 508 \pm 20 \text{ barns} \\ \sigma_c = 58 \text{ barns} \end{array} \right\} 2200 \text{ m/sec}$$

[η , σ_a , and σ_{fiss} represent conservative estimates of the probable errors.] Previous measurements of some of these constants have been made by Anderson and May.³ The principal differences found in this work are in the values of σ_a and σ_{fiss} .

5. APPENDIX

5.1 Determination of Isotopic Concentration of U^{233} Samples. A sample of U^{233} was submitted to A. J. Dempster for mass-spectrographic analysis. This result⁴ coupled with counting data taken by E. K. Hyde of Katzin's group led to the conclusion that the specific activity of U^{233} element counted in a 52 per cent geometry is 10,900 c/min per gamma. The isotopic concentration of all further samples was then obtained solely by alpha counting in this geometry.

5.2 Microplating Technique Used at Argonne. Foils containing from 12 to 48 μg of U^{233} as U_3O_8 were prepared at Argonne by an electrodeposition technique. An acid-free solution of $UO_2(NO_3)_2 \cdot 6H_2O$ was prepared by dissolving a weighed sample of U_3O_8 in HNO_3 and boiling off all the acid. The residue was then dissolved in a measured volume of water.

Aliquots of from $\frac{1}{2}$ to 1 cc were placed on the foils, which were then set on a ceramic plate on top of a hot plate. A fine platinum wire was used as the positive electrode with the foil as the negative one and a potential of 6 volts between them. The drop of solution was probed with the wire, which was kept in constant motion, until the drop evaporated down to near dryness. As this process took several minutes with most of the plating taking place in the first 30 sec, the use of this technique assured the deposition of all the material. The uniformity of plating was indicated by the small number of interference fringes produced by the U_3O_8 film.

5.3 Supplementary Experiment to Check Values of the Resonance Correction. The following experiment which would give a value for $\eta(U^{233})/\eta(U^{235})$ by the swing method and yet be independent of the cross sections of U^{233} and U^{235} for resonance neutrons was devised: A hollow rectangular parallelepiped made of cadmium was placed at the center of the stringer used for the oscillating samples, so that the sets of cans would be within the cadmium chamber when in measuring position. The effect of this was to depress the flux in the region of the cadmium. Measurements of relative fast-neutron flux along the stringer were made with cadmium-clad copper foils. By plotting the values so obtained, two points, 3 ft from center, were found at which the fast flux was the same as at the center of the stringer.

The sample cans were now oscillated between these points and center. Since the fast flux was identical at all three points, the swings were due to the effects of the capture of thermal neutrons only.

Sets of U^{233} , U^{235} , and B cans were swung in turn against the dummy set. By thus eliminating the need for the resonance correction, the swings were represented by

$$S_{U^{233}} = K n v N_{U^{233}} \sigma_{U^{233}} (\eta_{U^{233}} C - 1)$$

$$S_{U^{235}} = K n v N_{U^{235}} \sigma_{U^{235}} (\eta_{U^{235}} C - 1)$$

$$S_B = K n v N_B \sigma_B (-1)$$

Since the value of the factor C was changed by the insertion of the cadmium, $\eta_{U^{233}}$ and $\eta_{U^{235}}$ could not be calculated directly, but $\eta_{U^{233}}/\eta_{U^{235}}$ could be obtained by elimination of C and K n v from the above equations:

$$\frac{\eta_{U^{233}}}{\eta_{U^{235}}} = \frac{N_{U^{235}} \sigma_{U^{235}}}{N_{U^{233}} \sigma_{U^{233}}} \left[\frac{S_{U^{233}} - S_B \frac{N_{U^{233}} \sigma_{U^{233}}}{N_B \sigma_B}}{S_{U^{235}} - S_B \frac{N_{U^{235}} \sigma_{U^{235}}}{N_B \sigma_B}} \right]$$

The observed swings were

$$S_{U^{233}} = 43.2$$

$$S_{U^{235}} = 33.25$$

$$S_B = -50.15$$

Using the previously obtained values for $N\sigma$, these swings gave a value of 1.10 for $\eta_{U^{233}}/\eta_{U^{235}}$, which agrees with the ratio of the values of $\eta_{U^{233}}$ and $\eta_{U^{235}}$ as obtained by the original swing measurements. This indicates that the accepted values for the resonance correction could not be much in error.

5.4 Supplementary Experiment to Check Value of the Resonance Escape Probability. Swing measurements were made in an all-graphite section of the pile by removing the pile lumps from the region used. The increase in moderator path from the samples to the nearest pile lumps raised the resonance escape probability effectively to unity. This change also affected the other two factors which enter into C , but a recalculation of them made possible the verification of the accepted value for the resonance escape probability by a comparison of the values of η obtained in this and in the original swing measurements.

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Table 1

Cell No.	Grams U_3O_8	Isotope	Isotopic conc., %	Area, cm^2	Grams	U^{233} or U^{235}		Grams	U^{233}		Grams	O	
						Atoms $\times 10^{-20}$	Atoms/ cm^2 $\times 10^{-20}$		Atoms $\times 10^{-20}$	Atoms/ cm^2 $\times 10^{-20}$		Atoms $\times 10^{-20}$	Atoms/ cm^2 $\times 10^{-20}$
1	0.08244	233	94.9	0.1703	0.06607	1.708	10.03	0.00363	0.092	0.540	0.01274	4.796	28.16
2	0.08253	235	82.8	0.1702	0.05773	1.480	8.696	0.01214	0.307	1.804	0.01266	4.765	28.00
3	0.03586	233	96.2	0.1703	0.02914	0.7532	4.423	0.00117	0.0296	0.174	0.00555	2.089	12.27
4	0.32512	233	96.2	0.6732	0.2642	6.829	10.14	0.01063	0.2690	0.3996	0.05030	18.93	28.12
5	0.3252	235	83.2	0.6735	0.2286	5.859	8.699	0.04673	1.183	1.756	0.04988	18.77	27.87

Table 2

Measure- ment No.	Cell No.	Isotope	T	$-\ln T - \Sigma N\sigma_s$	β	$N\sigma_a$]kT	σ_a]kT	v , m/sec	σ_a] 2200 m/sec, barns
1	1	233	0.5518	0.5744	0.983	0.5645	562.8	2128	544
2	2	235	0.5495	0.5786	0.984	0.5688	654.1	2130	633
3	4	233	0.5355	0.6044	0.987	0.5965	588.2	2150	575
4	3	233	0.7567	0.2697	0.936	0.2524	569.8	2150	557
5	4	233	0.5282	0.6181	0.989	0.6112	602.8	2150	589
6	4	233	0.5490	0.5794	0.984	0.5700	562.1	2150	549
7	4	233	0.5321	0.6107	0.988	0.6033	595.0	2155	583
8	5	235	0.5454	0.5862	0.985	0.5771	663.4	2155	650

Average $\sigma_a(U^{233})kT = 580.1$ Average $\sigma_a(U^{235})kT = 658.8$ Average $\sigma_a(U^{233}) = 566$ Average $\sigma_a(U^{235}) = 642$

Table 3—Contents of Cans for Swing Measurements (Five Cans per Set)

Set	Weight of cans, g	Weight of Al powder, g	Weight of U_3O_8 , g	Breakdown of results
U^{233}	8.2880	1.4484	0.07859	96.2% U^{233} ; 0.3193 g of U^{233} ; 8.254×10^{20} atoms of U^{233}
	8.2874	1.4477	0.07856	
	8.2855	1.4458	0.07845	
	8.2853	1.4509	0.07873	
	8.2851	1.4506	0.07871	
	41.4313	7.2434	0.39304	
U^{235}	8.2884	1.4379	0.07816	82.8% U^{235} ; 0.2750 g of U^{235} ; 7.048×10^{20} atoms of U^{235}
	8.2875	1.4389	0.07821	
	8.2858	1.4422	0.07839	
	8.2852	1.4369	0.07810	
	8.2850	1.4411	0.07833	
	41.4319	7.1970	0.39119	
Dummy	8.2873	1.4607	Weight of pyrex powder, g	2.066% was due to im- purities from grind- ing, leaving 2.720 g of pyrex
	8.2870	1.4609		
	8.2862	1.4612		
	8.2856	1.4604		
	8.2852	1.4607		
	41.4313	7.3039		
Pyrex	8.2870	1.4620	0.05555	
	8.2867	1.4614	0.05553	
	8.2865	1.4620	0.05555	
	8.2857	1.4620	0.05555	
	8.2854	1.4613	0.05552	
	41.4313	7.3087	0.2777	

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Table 4

Position											
Sample	Dummies	Sample	Average swings*						Average	$\Delta ih^\dagger$	
U ²³³	South	North	36.9	36.5	35.5				36.3		
U ²³³	North	South	36.9	37.4	37.9				37.4		
										73.7	
U ²³⁵	South	North	26.7	25.9	26.7				26.4		
U ²³⁵	North	South	28.8	28.5	28.6				28.6		
										55.0	
Pyrex	South	North	-35.9	-38.2	-38.7	-36.8	-36.6	-34.7	-36.8		
Pyrex	North	South	-29.4	-29.1	-28.1	-30.0	-31.2	-31.1	-29.8		
										-66.6	

*Each entry is the average of twenty swings; sample set of swings follows:

North - dummies	North - dummies	North - U ²³³	North - U ²³³
South - U ²³³	South - U ²³³	South - dummies	South - dummies
37.8	34.7	36.4	37.8
34.0	36.4	35.4	37.1
34.3	38.7	35.8	36.7
37.1	39.4	35.2	38.5
36.8	40.9	35.6	38.4
38.5	40.8	35.9	36.0
38.6	38.5	35.8	36.5
36.0	36.9	35.9	36.9
36.4	37.5	36.1	36.3
36.3	38.8	36.6	36.5
Average	37.4	Average	36.5

$^\dagger \Delta ih \sim \text{total.}$

Table 5

Material in cell	Total counts
U^{238}	71,341
U^{235}	97,768
U^{233}	102,498
U^{238}	71,237
U^{235}	98,014
U^{233}	102,060
U^{238}	71,155
U^{235}	98,158
U^{233}	102,015
U^{238}	71,293
U^{235}	98,129
U^{233}	102,521

Totals: $U^{238} = 285,026$

$U^{235} = 392,069$

$U^{233} = 409,094$

$U^{235} - U^{238} = 107,043$

$U^{233} - U^{238} = 124,068$

Ratio 233/235 = 1.159

Table 6

Cd ratio	Distance of counter from cell, cm	$U^{233} - U^{238}$, counts	$U^{235} - U^{238}$, counts	U^{233}/U^{235} ratio
28×10^3	10	124,068	107,043	1.159
28×10^3	20	73,473	65,189	1.127
28×10^3	30	31,391	27,541	1.140
28×10^3	40	21,518	18,610	1.156
90×10^3	20	9,734	8,520	1.142

Weighted average* 1.147

*Each ratio value weighted by the number of counts.

Table 7

Foil	Atoms of U^{233}	Gain 17 c/m-A*	Gain 18 c/m-A*	Gain 19 c/m-A*	Gain 20 c/m-A*
U^{233} -a	2.332×10^{16}	4.416	4.473	4.438	4.511
U^{233} -b	7.773×10^{16}	4.493	4.512	4.489	4.477
U^{233} -c	15.90×10^{16}	4.407	4.411	4.428	4.414
Average		4.439	4.465	4.452	4.467
Atoms of U^{235}					
U^{235} -a	1.681×10^{16}	5.015	4.999	4.989	4.997
U^{235} -b	2.520×10^{16}	4.798	4.825	4.821	4.877
U^{235} -c	3.362×10^{16}	4.884	4.946	4.926	4.938
Average		4.889	4.919	4.907	4.933
$\frac{\sigma_{fiss}(U^{233})}{\sigma_{fiss}(U^{235})} = \frac{c/m-A(U^{233})}{c/m-A(U^{235})} =$		0.9080	0.9077	0.9073	0.9056

Total number of counts

> 0.5×10^6 on U^{235} foils> 1.3×10^6 on U^{233} foils

*c/m-A = fission counts per atom divided by monitor counts in arbitrary units.

Table 8

U^{233} set		U^{235} set	
Foil No.	μg of element	Foil No.	μg of element
1	15.5	1	12.6
2	30.9	2	25.2
3	46.4	3	42.0
4	35.6	4	27.1

Table 9*

Foil	Total counts/min for complete cycle	Total counts/min μg	$\frac{U^{233}}{U^{235}} = \frac{\sigma_{fiss}(U^{233})}{\sigma_{fiss}(U^{235})}$
$U^{233}-1$	148,845	9,603	
$U^{235}-1$	128,336	10,185	0.943
$U^{233}-2$	148,384	4,802	
$U^{235}-2$	128,027	5,080	0.945
$U^{233}-3$	415,283	8,950	
$U^{235}-3$	389,404	9,272	0.965
$U^{233}-4$	645,980	18,150	
$U^{235}-4$	512,220	18,908	0.960
Average			0.953

*Total number of counts in determination $>15 \times 10^6$.

Table 10*

Chamber 1		Chamber 2		$\frac{U^{233}}{U^{235}}$
Foil	Counts/ μg	Foil	Counts/ μg	
$U^{233}-5$	2232	$U^{235}-5$	2386	0.9354
$U^{235}-5$	2413	$U^{233}-5$	2244	0.9300
$U^{233}-6$	2218	$U^{235}-6$	2434	0.9112
$U^{235}-6$	2430	$U^{233}-6$	2220	0.9136
Average				0.9226

*Total number of counts in determination $>1 \times 10^6$.

Fig. 1a—Steel cell to contain powdered samples.

Fig. 1b—Loaded cell showing plunger used to press contents firmly.

Fig. 2—Sliding mount for accurate and rapid interchange of the cells.

Fig. 3—Optical bench.

Fig. 4—Dilution apparatus to reduce self-protection.

DIMENSIONS ARE IN INCHES

Fig. 5a—Schematic diagram showing position of cans relative to the center of the pile.

Fig. 5b—Schematic diagram showing swing setup.

Fig. 6—Long-counter mounting arrangement.

Fig. 7—Quick-opening fission chamber.

Fig. 8— Graph of micrograms of fissionable element on the foils against counting rate.

Fig. 9—Graph of micrograms of fissionable element on the foils against counting rate.

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Paper 3.1

VOLATILIZATION OF PROTACTINIUM FROM THORIUM IN A STREAM OF HYDROGEN FLUORIDE

By Paul A. Schulze

[Editor's Note: The investigation reported in this paper was undertaken at the suggestion and under the supervision of R. W. Stoughton. The paper is a contribution from the Argonne National Laboratory and is based on Report CB-3745.]

1. INTRODUCTION

Uranium²³³ essentially free of natural uranium can be obtained from the neutron bombardment of thorium

in two ways: (1) total decay of Th^{233} to U^{233} , separation of uranium from thorium (sufficient bombardment necessary so that the amount of natural uranium is an insignificant part of the total uranium present); or (2) separation of Pa^{233} from both thorium and uranium and subsequent decay of Pa^{233} to U^{233} (completely free of natural uranium).

The second way is essential where low concentrations of U^{233} are formed.

Von Grosse¹ reported that protactinium pentachloride sublimes to an appreciable extent below its melting point of 301°C, and Brown and Hill² reported that 95 per cent of the protactinium activity dispersed in a uranium dioxide sample was volatilized by passing gaseous anhydrous hydrogen fluoride over the sample at a temperature of 500°C for 30 min. Since both uranium tetrafluoride and thorium tetrafluoride are relatively nonvolatile at 500°C, a fluoride volatilization procedure or the isolation of Pa^{233} seemed promising.

2. APPARATUS

An all-copper system was used. The reaction chamber was heated by an electric furnace, and the temperature was measured with a chromel-alumel thermocouple placed in an inside well.

3. MATERIAL

Commercial anhydrous hydrogen fluoride in tanks was used. Half-life measurements of the protactinium samples used gave values from 27 to 29 days. Both the carrier samples of solid thorium oxalate containing Pa^{233} , previously prepared by R. W. Stoughton, and the cyclotron-bombarded samples of thorium hydroxide and thorium oxalate were slurried in water. The thorium hydroxide carrier samples were prepared by treatment of a solution of thorium nitrate containing Pa^{233} with NH_4OH . The protactinium solution had been prepared by R. W. Stoughton by electrolytic isolation of the protactinium and subsequent dissolution in nitric acid.

4. PROCEDURE

In general, the slurry was transferred to a platinum plate and slowly evaporated to dryness on an electric hot plate. The activity of the dried slurry was determined with a Geiger-Mueller counter, and, in the case of low activity, corrections for thorium background were made. The platinum plate was set upon a copper disk and both were placed in the copper reactor as near as possible to the inside thermocouple well. Continuous passage of gaseous anhydrous hydrogen fluoride was maintained through the reactor (1) while the air was displaced from the cold reactor, (2) while the reactor was rapidly heated to temperature for the desired length of time, and (3) during cooling of the reactor. Although no measurement of the anhydrous hydrogen fluoride flow rate was made, a constant flow was ensured by observing the faint cloud, produced by anhydrous hydrogen fluoride absorbing moisture from the air, emitted from the exit tube of the copper apparatus.

5. DISCUSSION

Curves I and II of Fig. 1 and curve IV of Fig. 2 show the volatilization of protactinium from thorium carrier compounds. Curves III and V show the volatilization of protactinium from cyclotron-bombarded thorium compounds.

Comparisons of curves I and II show that the kind of thorium carrier had no influence on the protactinium volatilization. Although no weighings were made of the amount of thorium oxalate used, a visual comparison of the oxalate and the hydroxide samples indicated that the weight of oxalate was probably over twice that of the hydroxide. Thus within this range the amount of carrier had little effect on this rough measurement of volatility. It must be emphasized that these volatility measurements may differ considerably from those with pure protactinium tracer or with microgram amounts of protactinium.

Curve IV indicates that 100 per cent volatilization of tracer protactinium should occur after about 100 min at a temperature of 475°C with about 2 mg of thorium oxalate carrier.

Some reasons for the difference between the protactinium behavior in the cyclotron-bombarded samples and the carrier samples are suggested by comparison of curves I and III and also IV and V. These reasons may be (1) that the carrier sample is more easily fluorinated because the protactinium is adsorbed on the outside of the solid thorium compound, whereas the protactinium in the cyclotron-bombarded sample is distributed randomly throughout the thorium compound and thus can only be fluorinated when the thorium compound is completely converted to ThF_4 ; or (2) that a relatively nonvolatile protactinium compound, alone or mixed with the volatile fluoride ($\text{PaF}_5?$), is formed. Possible protactinium compounds of this type are PaOF_3 and a fluoride of an oxidation state less than +5.

In an effort to determine whether a reduced state was responsible for the lower volatilization in the cyclotron-bombarded samples, some samples of cyclotron-bombarded material, before treatment with anhydrous hydrogen fluoride at 600°C , were dried on a hot plate at low heat while others were heated in air for an additional 4 hr at 250°C .

The data in Table 1 would seem to indicate that a reduced state may be present in the cyclotron-bombarded samples.

6. SUMMARY

Protactinium dispersed in thorium carrier compounds is volatile in a stream of gaseous hydrogen fluoride at temperatures over 450°C . A possible valence state of less than +5 for protactinium is suggested by a lower volatilization of protactinium in cyclotron-bombarded thorium compounds, as compared to the volatilization of the protactinium in thorium carrier compounds.

Table 1—Volatilization of Protactinium from Cyclotron-bombarded Samples

Initial treatment	% volatilized at 600°C in HF stream	
	60 min	120 min
Normal drying	53	72
	76	75
	64	83
	76	
	78	
	Av. 70	Av. 77
Heating in air	90	84.5
	91	84
	92	89
	Av. 91	Av. 86

Fig. 1—Effect of temperature on volatilization of Pa from Th in a stream of HF. ○, 1 mg $\text{Th}(\text{OH})_4$ carrier for 30 min. ●, 2 mg $\text{Th}(\text{C}_2\text{O}_4)_2$ carrier for 30 min. x, cyclotron-bombarded $\text{Th}(\text{OH})_4$ for 30 min (about 2 mg).

Fig. 2—Rate of volatilization of Pa tracer from Th in HF stream. $\circ$, cyclotron-bombarded $\text{Th}(\text{OH})_4$ at 600°C (about 2 mg). $\bullet$, 2 mg $\text{Th}(\text{C}_2\text{O}_4)_2$ carrier at 475°C .

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Paper 3.2

A MANGANESE DIOXIDE PROCEDURE FOR ISOLATION AND CONCENTRATION OF PROTACTINIUM FROM IRRADIATED THORIUM COMPOUNDS

By Leonard I. Katzin and Raymond W. Stoughton

[Editor's Note: This paper is a contribution from the Chemistry Division, Argonne National Laboratory, and is based on work performed in the interval April to September 1943 and recorded in Reports CC-739 and ANL-4035.]

1. INTRODUCTION

Thorium is used as the target material in neutron or deuteron irradiations designed to yield the synthetic isotopes of uranium, U^{232} and U^{233} . The initial reaction product may be either a thorium isotope or a protactinium isotope, but in neither case is the uranium nucleus formed directly. In most cases the concentration of product isotopes is a minute fraction of a part per million of the original thorium. Since this thorium may contain in the neighborhood of one to several parts per million of natural uranium impurity, it is impractical to obtain pure synthetic uranium isotopes by allowing decay of the intermediate protactinium and then separating out uranium. It is accordingly necessary to investigate the isolation of the intermediate protactinium and its freeing from natural uranium as well as from thorium.

A method which has already been applied to the separation of protactinium from irradiated thorium salts is based on the coprecipitation of protactinium with manganese dioxide.¹ It is the purpose of this paper to give the results of studies on the conditions for this separation, the efficiency of separation from thorium and uranium, and the possibilities of a concentration process which does not involve the use of alternate carriers such as zirconium phosphate.

2. EXPERIMENTAL WORK

The system chosen was a solution of thorium nitrate containing nitric acid and manganous nitrate in excess. The desired amount of manganese dioxide (usually 1.5 g per liter) was precipitated by the addition of the proper amount of potassium permanganate. A digestion with warming was usually allowed. Experiments were customarily performed with solutions of 0.1 ml total volume, the precipitate being separated by centrifugation. Reagents were added, and supernatants were removed with the aid of glass capillaries. For determination of the behavior of the tracers used (Pa^{233} and UX_1), material was mounted on platinum disks and measured with the Geiger-Mueller counter (having a thin-mica end window) standard in the laboratory.

The completeness of the manganese dioxide precipitation and the physical characteristics of the precipitate were shown to be dependent on the nitric acid concentration. The range from less than 1N to 4N or 5N was shown to be safe by experiments in which macro quantities of the dioxide were precipitated and the manganese in the precipitate was determined. The concentration of thorium nitrate also affected the precipitation strongly in the higher ranges of thorium concentration, in large part by affecting the physical properties of the solution. The range up to 360 g of thorium nitrate tetrahydrate per liter (0.65M) was found to give good precipitation of the manganese dioxide, while at twice this concentration it was poor.

With the aid of UX_1 tracer, the carrying of thorium on the manganese dioxide was also determined. As the results show (Table 1), the carrying is a function of thorium concentration, with trace concentrations of thorium being carried essentially completely. Detectable amounts of thorium are carried by manganese dioxide from concentrations of thorium nitrate in the normal range (0.02M to 0.65M). This can be demonstrated by dissolving the washed precipitate in hydrogen peroxide, which gives a residue of insoluble thorium peroxide compound. In addition to the thorium itself, members of its decay chain are carried fairly well. This produces a background of radioactivity in tracer experiments which must be taken into consideration. The principal activities carried seem to be ThB and ThC, the latter in an amount two or three times that which would normally be in radioactive equilibrium with the former. Others have since found that the carrying of UX_1 tracer is decreased, without affecting protactinium carrying,² by increasing nitric acid concentration.

Protactinium tracer was found to be carried well by manganese dioxide in the range of optimal precipitation. Yields of over 95 per cent could be demonstrated by slurring the precipitate onto platinum

counting disks for measurement. Lower recoveries (75 to 90 per cent) were found when the precipitate was dissolved in the centrifuge cone and the resulting solution was evaporated onto the counting disk. Some of the lost tracer could be recovered from the glassware used on washing with hydrofluoric acid, indicating that the loss occurs in the process of dissolving the manganese dioxide. This fact and the irregular adsorption of protactinium on glass rendered experimental results somewhat erratic.

Following a first precipitation of manganese dioxide from thorium solutions, the Pa^{233} carried is still quite dilute. It was thought that cycles consisting of manganese dioxide precipitation, dissolution of the precipitate in a small volume of reagent, and reprecipitation of a small fraction of the manganese by addition of permanganate could be used to achieve concentration and further purification simultaneously. Within the scale of operations available in the laboratory this proved feasible, and on the basis of these results a similar process was later applied to larger scale operations at the Clinton Laboratories.³

Since hydrochloric acid is undesirable for use in metal equipment, especially when chlorine will be formed from it, other agents were investigated for dissolving the manganese dioxide. The foaming of hydrogen peroxide was not a desirable characteristic for work with radioactive solutions, and the instability of the reagent was considered another drawback. Hydrogen peroxide also tended to form insoluble thorium peroxide with the coprecipitated thorium. Sodium nitrite reacted with freshly precipitated dioxide but was not satisfactory for work with commercial material. Formic acid was investigated and was shown to dissolve the dioxide well when heated. The number of factors entering into its use (rate of reaction, stability, gas evolution, etc.) made it only partially satisfactory. Hydroxylamine proved to be a good choice, however, reacting stoichiometrically even in the cold. Although the hydrochloride was used in the tests, it was not felt that the amount of chloride introduced would be of significance even in metal equipment.

Using hydroxylamine, it has been possible to obtain a concentration factor as high as 100 per cycle. Since such a factor rapidly alters the scale of operations, a considerably smaller one can be used satisfactorily. Experiments in which the manganese was reprecipitated without change of volume showed that four such precipitations could give as much as 80 to 85 per cent recovery. Experiments were also performed in which starting volumes of about 10 ml were reduced to 0.1 ml by the first cycle, with the second precipitation giving the activity on 0.15 mg or less of manganese dioxide. Yields of 85 per cent have been obtained through the two cycles of such experiments. In addition

to low-activity tracer experiments of this type, the procedure was tested on thorium oxycarbonate that had been exposed for a long time to slow neutrons produced in the St. Louis cyclotron. Starting with a volume of 10 to 15 ml of thorium nitrate solution, the Pa^{233} activity came satisfactorily with the manganese dioxide and was concentrated in the second precipitate as scheduled. Approximately $0.05 \mu\text{g}$ was concentrated readily in this fashion.

The eventual recovery of U^{233} following this procedure could be achieved through storing the last manganese dioxide precipitate to allow the desired protactinium decay, dissolving the manganese dioxide, and reprecipitating it. The precipitate would separate off most of the remaining protactinium radioactivity, allowing convenient recovery of the uranium from the supernatant by solvent extraction. The solvent extraction could be carried out without the precipitation of the protactinium, but it is rendered easier by prior removal of the radiation source, which might necessitate shielded operation. Experiments with U^{232} tracer showed that the carrying of uranium by manganese dioxide was low enough to give the required purification of the protactinium from the natural uranium impurity of the thorium irradiated originally.

3. SUMMARY

Traces of protactinium may be coprecipitated on manganese dioxide with good recovery from solutions 1N to 4N in nitric acid by precipitating 1.5 g of dioxide per liter by the addition of potassium permanganate to manganous nitrate in excess. Good separation is obtained from macro concentrations of thorium nitrate. In concentrations up to 0.65M the thorium does not interfere with the precipitation, while at twice this concentration definite interference is found owing to the effect on the physical properties of the solution. With the aid of hydroxylamine to redissolve the dioxide, it is possible to concentrate the protactinium with respect to carrier by a factor of 100 per cycle. Hydrogen peroxide, sodium nitrite, and formic acid were less satisfactory reagents. Simultaneous purification from thorium and uranium may be achieved.

Thorium is found to carry well in trace concentrations, but the efficiency of this process falls off with increasing thorium concentration.

Table 1 — Carrying of UX_1 Tracer by 1.5 g of MnO_2 per Liter
from Thorium Nitrate Solutions

Conc. thorium nitrate tetrahydrate, g/liter	Per cent UX_1 carried
0.1	99
10	20
120	5
360	0.3

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Paper 3.6

ISOLATION OF URANIUM WITHOUT CARRIER FROM THORIUM METAL BOMBARDED WITH DEUTERONS

By Roy Overstreet and Louis Jacobson

[Editor's Note: Contribution from the Metallurgical Laboratory, University of California. Prepared for publication January 1944.]

ABSTRACT

Two methods for the isolation of uranium in tracer amounts from deuteron-bombarded thorium were used: one by virtue of the formation of an NH_4OH -soluble complex of uranium with hydroxylamine, and the other by use of an oxidation-reduction cycle. In both methods the bulk of the thorium was removed by precipitation as the fluoride. In the hydroxylamine method, uranium was first precipitated with NH_4OH using Fe carrier. The precipitate was dissolved in HCl and again treated with NH_4OH , this time after the addition of hydroxylamine hydrochloride, thereby leaving the uranium in solution. Two more such series of treatments were sufficient to produce a pure sample. The other method consisted in reducing the uranium to the +4 state with a titanous salt and precipitating the uranous ion with HF using La^{+3} carrier. The uranium was then oxidized to the +6 state with HNO_3 and treated again with HF , this time remaining in solution. The cycle was repeated twice more.

1. INTRODUCTION

The methods described make use of the facts that hexavalent uranium forms a strong soluble complex with hydroxylamine in ammoniacal solutions and that quadrivalent uranium forms an insoluble fluoride in acid solutions.

For either method the deutron-bombarded thorium metal, which contains uranium, protactinium, and fission products, is dissolved in aqua regia, and the HCl is removed by boiling with HNO_3 . The thorium is then precipitated as the fluoride in 2N HF and 1N HNO_3 ; the precipitate is washed twice with 2N HF. By this procedure the combined filtrate and washings contain about 93 per cent of the uranium activity. The fluoride solution is evaporated to fuming with 1 cc of concentrated H_2SO_4 and then diluted to 20 cc.

2. HYDROXYLAMINE METHOD

In this procedure the uranium is precipitated as ammonium uranate using $\text{Fe}(\text{OH})_3$ carrier and leaving the NH_4OH -soluble constituents in solution. In the subsequent precipitation, in the presence of hydroxylamine, the NH_4OH -insoluble constituents are carried down with the iron, and the uranium remains in solution as the ammonia-soluble uranyl hydroxylamine complex.

Ten milligrams of Fe is added to the thorium-free solution. The solution is made strongly basic with NH_4OH and boiled. The $\text{Fe}(\text{OH})_3$ is centrifuged out, and the supernatant liquid is discarded. The precipitate is dissolved in 0.5 cc of concentrated HCl, and the solution is diluted to 30 cc. Concentrated NH_4OH is added to neutrality, and then 1 cc is added in excess. The mixture is heated to boiling and centrifuged; the supernatant liquid is discarded. The $\text{Fe}(\text{OH})_3$ is dissolved in 0.5 cc of concentrated HCl, and the solution is diluted to 30 cc.

One gram of hydroxylamine hydrochloride is added to the Fe solution, and the solution is made strongly basic with 5 cc of concentrated NH_4OH . The mixture is heated to boiling and then cooled rapidly to prevent excessive decomposition of the hydroxylamine. The iron hydroxide is centrifuged out, and the supernatant liquid is set aside. The Fe precipitate is dissolved in 0.5 cc of concentrated HCl and reprecipitated twice more in the presence of hydroxylamine as before. The Fe precipitate is then discarded, and the supernatant liquids containing the uranium are combined. The hydroxylamine is destroyed by evaporating the solution to a small volume and treating several times with aqua regia. The recovery of uranium from the cycle is about 95 per cent. For the complete removal of beta activity, it is desirable to carry the uranium solution through the cycle once or twice more.

3. THE REDUCTION METHOD

In the following procedure the uranium is reduced to the quadrivalent state by Ti^{+3} and precipitated as the fluoride with LaF_3 carrier

together with all other fluoride-insoluble constituents. Following this the uranium is oxidized to UO_2^{++} , which forms a soluble fluoride. The lanthanum and the other fluoride-insoluble constituents are then removed with HF.

The thorium-free solution (20 cc) is made 2N in H_2SO_4 . One cubic centimeter of 15 per cent TiCl_3 or $\text{Ti}_2(\text{SO}_4)_3$ is added, and the solution is heated on a steam bath for 10 min. The material is cooled, and 5 mg of La^{+3} is added. The solution is made 2N in HF and allowed to stand for 10 min. The precipitate is centrifuged out and washed with 1N HF; the supernatant liquid and washing are described. The precipitate is fumed with 1 cc of concentrated H_2SO_4 and then cooled. A few drops of concentrated HNO_3 are added, and the mixture is fumed again. The solution is diluted to 20 cc. In this procedure the recovery of uranium is 90 to 95 per cent.

The solution is made 2N in HF, and LaF_3 is centrifuged out and washed with 1N HF. The precipitate is discharged, and the supernatant fluid and washing are combined and evaporated to fuming. The solution is diluted to 20 cc. In this step the recovery of uranium is 95 to 100 per cent. For maximum purification it is desirable to repeat the entire cycle twice more.

Paper 3.7

FEASIBILITY OF SEPARATING U^{233} FROM THORIUM AND Pa^{233} BY SOLVENT EXTRACTION

By B. J. Fontana

[Editor's Note: Contribution from the Radiation Laboratory, University of California, Berkeley. Based on Report CC-3854 (rewritten from Report CC-384 by R. W. Stoughton). This work was carried out during the fall of 1942 at the Chemistry Department, University of California. Prepared for publication Dec. 19, 1947.]

1. INTRODUCTION

Uranium²³³ can be made from thorium and a neutron source according to the following series of reactions:

and the amounts of U^{233} that can be produced depend on the magnitude of the neutron source. As soon as the early results of an investigation¹ of some of the nuclear properties of U^{233} were obtained, it was obvious that methods for isolating U^{233} on a relatively large scale should be developed.

Preliminary results on precipitation methods were not very encouraging, since, of the compounds studied, the thorium salt in each case was less soluble than the corresponding uranyl salt; it is more advantageous in principle to precipitate the smaller component (here U^{233}) from the larger, rather than vice versa. Further, in view of the known high solubility of uranyl nitrate in diethyl ether, a solvent extraction procedure appeared worthy of serious consideration. Actually some evidence was already existent in this laboratory, since uranium

had been separated from its daughter Th^{234} (i.e., UX_1) by extraction of the former preferentially into ether, leaving the Th^{234} in the aqueous phase; this work was conducted by G. T. Seaborg, I. Perlman, et al. Also J. W. Kennedy and A. DeHaan, Jr., of this laboratory have found that increasing the concentration of uranium (as uranyl nitrate) up to 0.1 g/ml caused a corresponding increase in the preferential solubility in the ether phase. Little or no salting effect was observed in solutions of 1M and 3M NH_4NO_3 , 1M LiBr , and saturated NH_4Cl . In 6M HNO_3 , however, a constant partition ratio of about unity was observed over a range of uranyl concentration of a few micrograms to several hundred micrograms per milliliter.

Misciattelli has studied the ternary system of the anhydrous salts $\text{Th}(\text{NO}_3)_4$ and $\text{UO}_2(\text{NO}_3)_2$ in pure ether² and also the ternary systems $\text{Th}(\text{NO}_3)_4 - \text{H}_2\text{O} - \text{ether}$ and $\text{UO}_2(\text{NO}_3)_2 - \text{H}_2\text{O} - \text{ether}$.³ The results of these studies indicate a higher distribution coefficient (ether/aqueous) for uranium than for thorium under comparable conditions of salting-agent strength and also indicate that, in order to prevent excessive amounts of thorium from extraction, weight ratios of $\text{Th}(\text{NO}_3)_4$ to H_2O of less than unity should be employed in the aqueous phase.

The purpose of the investigation was to test the feasibility of separating U^{233} from thorium by solvent extraction. The efficiency of the method would depend of course on the relative magnitudes of the distribution coefficients of uranium (in small concentrations) and thorium (in relatively large concentrations) under conditions where the uranium distribution ratio is greater than about unity.

2. EXPERIMENTAL WORK

All experiments were performed at room temperature (about 20°C). In all cases 25 g of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ was used. The required amount of water was added to produce the desired ratio of $\text{Th}(\text{NO}_3)_4$ to H_2O , taking into account the water already present as water of hydration in the salt, i.e., $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$. This aqueous solution was then shaken with ether for about 10 to 15 min. The volume of the aqueous phase was measured before and after extraction. It was assumed that the volume increase in the ether phase was equal to the observed volume decrease of the aqueous phase. This assumption is very probably of the same order of accuracy as the analyses in these experiments; and actually it need only be applied in the experiments with almost saturated $\text{Th}(\text{NO}_3)_4$ solutions and in experiments in the presence of HNO_3 , which are of the least interest or practicability, as will be seen below.

The two phases had to be separated very cleanly in order that the thorium distribution might be determined with any accuracy, since the amount of salt in the ether phase weighed as little as 0.02 g as

compared to 25.0 g in the aqueous phase. The thorium in the ether phase was determined simply by evaporation of the ether, first with added H_2O , then with added HNO_3 (when all the ether was gone), to dryness on a steam bath. Under these conditions the residue corresponds to $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ and was merely weighed as such.

Obviously it was convenient to analyze only the ether phase for uranium. The thorium in the residue from the evaporation of the ether phase was then separated from the uranium present by precipitation as thorium fluoride with a slight excess of HF . Where necessary, a second precipitation was performed after evaporation of the supernatant solution to dryness with HNO_3 in a platinum dish. These precipitations were carried out at concentrations of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ ranging from 0.02 to 0.002 g/ml (except in one experiment, at 0.05 g/ml). It was assumed in all cases that 100 per cent of the uranium remained behind in the supernatant solution. Actually, results by Stoughton⁴ indicate that at a concentration of about 0.05 g of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ per milliliter tracer amounts of uranium are carried by thorium fluoride on addition of HF , to the extent of about 10 per cent.

In one experiment about 50 mg of uranium was used. Analysis in this case was gravimetric, the uranium being precipitated with NH_4OH and ignited to U_3O_8 . The remaining experiments were conducted with either 1 to 2 mg of uranium or tracer amounts of U^{232} . Colorimetric methods of analysis for the milligram quantities of uranium were unsuccessful. Traces of impurities in the various reagents gave interfering colors. A method of fluorescent analysis was finally used. The intensity of the fluorescence produced by illuminating the sample, which is incorporated into a phosphoric acid glass, with ultraviolet light is measured with a photoelectric cell. Comparison with standards gives the desired analysis. Our particular setup conveniently detected from 2 to 0.1 mg of uranium, and the accuracy was at best about 10 per cent.

The tracer experiments, which are probably the most reliable, employed U^{232} , a 70-year alpha emitter. An amount of tracer was used in each experiment which gave about 2200 c/min. The actual uranium content of this tracer is unknown, being dependent solely upon the original uranium impurity in the thorium used for the preparation of the tracer, i.e., by the reaction

It is very improbable, however, that the amount used in each experiment contained any more than 1 μg of uranium. The samples (ether

phases) were evaporated onto platinum disks for counting. The weight of this evaporated residue was determined in each case; it varied from about 2 to 0.1 mg/cm². Self-absorption corrections were made where necessary. Blank experiments, of course, had to be performed, of which more will be said in the discussion of the actual results obtained. In all but one of the experiments with U²³² tracer, Pa²³³ tracer was also added, in order at the same time to determine the extractability of Pa²³³. The amount of the beta-emitting tracer (27.4-day half life) used in each experiment gave a deflection of about 2 div/sec on the Lauritsen electroscope used.

3. RESULTS

The calculated average partition coefficients, with the observed average deviation, for uranium and thorium are tabulated in Table 1 as a function of the initial weight ratio, R , of $\text{Th}(\text{NO}_3)_4$ to H_2O . The symbol k is the ratio of concentration in the water layer to concentration in the ether layer and hence becomes smaller in magnitude as the recovery in the ether phase increases. The corresponding normality, N , of the initial $\text{Th}(\text{NO}_3)_4$ solution, i.e., molarity of nitrate ion, is also given as total equivalents per liter of $\text{Th}(\text{NO}_3)_4$ or $\text{Th}(\text{NO}_3)_4$ plus HNO_3 . The experimentally observed density, d , in grams per cubic centimeter of these solutions, is also given as possibly being of interest. It might be noted in passing that, within the accuracy of determinations (± 2 per cent), the "apparent molal volume" of the $\text{Th}(\text{NO}_3)_4$ in all the solutions listed in Table 1 is constant at 102 cc per mole.

The observed experimental data are tabulated in Tables 2A and B; the former shows the extraction of uranyl and thorium nitrates into ether, while the latter shows the blank correction required for alpha and beta activity due to thorium-disintegration products. The practical significance of the results tabulated in Tables 1 and 2A is perhaps better grasped by referring to Fig. 1. Here all the data have been reduced to a common basis by plotting the per cent of uranium and thorium which would be extracted in each case in one extraction with an initial volume of ether equal to the initial volume of the aqueous phase versus N . It is to be noted from the data of Tables 2A and B that significant volume changes of the two phases occurred, upon mixing, only in the most concentrated $\text{Th}(\text{NO}_3)_4$ solution used, $R = 1.78$, and in the experiments in the presence of HNO_3 . Each individual experiment is plotted in the case of the uranium recovery, whereas only the average recovery of thorium is shown.

Figure 1 reveals immediately that in going from $R = 0.74$ to $R = 1.78$ the recovery of uranium rises rapidly from about 50 per cent at

$R = 0.74$ to a maximum of about 80 per cent at $R = 1.40$, the recovery then leveling off at 80 per cent or perhaps even dropping slightly as $R = 1.78$ is reached. The thorium recovery concurrently rises steadily, a relatively enormous increase occurring, from less than 0.1 per cent at $R = 0.74$ to about 20 per cent at $R = 1.78$. A point calculated from the data of Misciatelli on the ternary system $\text{Th}(\text{NO}_3)_4 - \text{H}_2\text{O} - \text{ether}$ is seen to be in good agreement with the thorium recovery data obtained here. Apparently the region of most promise for application to a method of uranium recovery is at about $R = 1.00$ (or lower), where less than 0.5 per cent of the thorium is extracted and about 70 per cent of the uranium is obtained in one extraction with equal volumes of the two phases. The several experiments done at $R = 0.74$ indicate that the uranium-partition coefficient is apparently independent (within the accuracy of the experiments) of the number of extractions performed, of the ratio of volumes of the two phases, and of the concentration of uranium, provided the latter is present in relatively small amounts. In these experiments the uranium varied from a total of about 50 mg to tracer amounts (probably less than $1 \mu\text{g}$), all in the presence of 10,500 mg of thorium.

It was thought necessary to determine the effect of HNO_3 on this system, since $\text{Th}(\text{NO}_3)_4$ as such is not likely to be used in the preparation of the U^{233} . If, for example, thorium hydroxide or oxide is used, it would have to be converted to the nitrate before this extraction method could be used. It is obviously desirable then to know whether the excess HNO_3 used in the conversion needs to be removed or not. The interesting result is noted (see especially Fig. 1) that, if the concentration of the aqueous phase is considered as total equivalents of $\text{Th}(\text{NO}_3)_4$ or $\text{Th}(\text{NO}_3)_4 + \text{HNO}_3$, the recovery of uranium in the presence of HNO_3 appears to fall on the same curve obtained in the absence of HNO_3 . This is further substantiated by a result obtained by DeHaan and Kennedy in 6N HNO_3 in the absence of any thorium whatsoever, which again seems to fall on the same curve. The presence of HNO_3 , however, is seen to be undesirable because of the greatly increased thorium recovery in the ether phase. This latter effect of HNO_3 on the thorium partition between water and ether is in qualitative agreement with the results obtained by Imre.⁵ Quantitative agreement with the latter data is probably not to be expected since Imre's experiments were done in relatively dilute $\text{Th}(\text{NO}_3)_4$ solutions. The experiment in HNO_3 at $N = 11.30$ [for a saturated aqueous $\text{Th}(\text{NO}_3)_4$ solution, $R = 1.8$, $N = 11.20$] indicates a still further increase in the thorium recovery and a very surprising drop in the uranium recovery. The latter drops from about 80 per cent at $N = 10.80$ with no HNO_3 present to about 34 per cent at $N = 11.30$ with a HNO_3 con-

centration of 6N. This effect has not been confirmed since this region is actually of no practical interest.

The particular stock of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ used was found to emit approximately $2\frac{1}{2}$ alpha particles per Th^{232} alpha. The 25-g samples of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ used in each experiment then must show about 2×10^6 c/min and of the order of 1 to 2 div/sec (on a Lauritsen electroscope) of beta activity arising solely from the thorium-disintegration series. The results obtained in Table 2B indicate that the combined ether extraction and fluoride precipitations result in a very complete separation of the uranium from the thorium-disintegration series as well as from the thorium itself. It is surprising that the former separation occurs with about the same efficiency regardless of the amount of thorium which goes into the ether phase during the extraction process or of the presence of HNO_3 . The observed activities noted in Table 2B were usually measured from 2 to 4 days after the time of ether extraction. The alpha activity decayed slowly, in a few days, to a value of alpha about half that noted in the table, and the beta activity was of the order of thousandths of a division per second in 1 or 2 days after the first measurement.

The specificity of the extraction process for uranium is brought out even more markedly in the experiments with Pa^{233} tracer (see Table 2A). Recall that in each experiment an amount of protactinium tracer amounting to about 2 div/sec was used. The final observed beta activity in every case, regardless of the per cent thorium extracted or of the presence of HNO_3 , was of exactly the same order of magnitude as the blank beta activities noted in Table 2B. This indicates that protactinium of the order of 0.1 per cent or less comes through with the extracted uranium. And, further, this uranium-protactinium separation must be due only to the ether extraction process since Stoughton has shown that, under the conditions employed herein, over 90 per cent of the protactinium will follow the uranium in a thorium-uranium separation by HF precipitation.

4. SUMMARY

The ether extraction method for separation of minute amounts of uranium from large amounts of thorium nitrate (and minute amounts of Pa^{233} if present) has been found to be a practical procedure. The uranium is found to favor the ether phase under conditions wherein the thorium is in quite concentrated aqueous solution, with little thorium and less Pa^{233} extracted. The presence of nitric acid is undesirable in that it increases the amount of thorium extracted by the ether but has no other deleterious effects within a reasonable limit of concentration. The uranium partition is independent of the concen-

tration of uranium over a wide range (of relatively low concentrations) and of the number of extractions made. The ether extraction also apparently effects a separation of uranium from the thorium-disintegration series under all the above conditions.

Table 1

R	N	d	k_U	k_{Th}
0.74	5.32	1.50	1.1 ± 0.2	1620 ± 220
1.00	6.84	1.64	0.50 ± 0.13	243 ± 18
0.74(2N HNO ₃)	7.32	1.56	0.40	14 ± 0
1.40	9.04	1.86	0.26 ± 0.03	25 ± 5
1.78	10.80	2.02	0.36 ± 0.07	5.2 ± 0.3
0.74(6N HNO ₃)	11.32	1.64	4.0	3.6

Table 2

A. Extraction of $\text{UO}_2(\text{NO}_3)_2$ and $\text{Th}(\text{NO}_3)_4$ into Diethyl Ether from Aqueous Solutions of $\text{Th}(\text{NO}_3)_4$ and $\text{Th}(\text{NO}_3)_4$ plus HNO_3^*

R	U	E/W initial	n	E/W final	% U	k_U	% Th	k_{Th}
0.74	48	0.735	2		68	0.97		
	1	0.735	1		35	1.36		
	2	1.00	2		77.5	0.90		
	2	0.50	4		79	1.04		
	2	1.00	1		40	1.5	0.06	1560
	Tracer†	1.00	1		52.2	0.92	0.08	1240
(6N HNO_3)	1	1.00	1	2.1	34	4.0	37	3.6
(2N HNO_3)	Tracer†	1.00	1	1.22	75.4	0.40	8.2	14
1.00	1	1.00	1		59	0.69	0.40	250
	1	1.00	1		73	0.37	0.40	264
	Tracer	1.00	1		69.4	0.44	0.47	216
1.40	1	1.00	1	1.05	79	0.28	3.3	30
	Tracer†	1.00	1	1.02	81.5	0.23	4.9	20
1.78	2	1.00	1	1.29	75	0.43	19	5.5
	Tracer†	1.00	1	1.32	82	0.29	22	4.8

B. Extraction of Thorium-disintegration Products into Diethyl Ether*

R	U	E/W initial	n	E/W final	α	β	% Th	k_{Th}
0.74	0	1.00	1		57	0.009	0.06	1560
	0	1.00	1		44	0.006	0.06	1670†
			1		52	0.006	0.04	2230
	0.001	1.00	1		47		0.07	1470
(2N HNO_3)	0	1.00	1	1.22	46	0.004	8.1	14
1.78	0	1.00	1	1.23	23	0.003	16	6.4

*Note: R = initial weight ratio of $\text{Th}(\text{NO}_3)_4$ to H_2O .

U = total weight of U in mg.

E/W = volume ratio of ether to water (before and after mixing; blank space indicates no appreciable change in latter case).

n = number of successive extractions from same aqueous starting solution.

% U, % Th = observed % recovery of U and Th, respectively, in the ether phase.

k_U , k_{Th} = partition coefficient for U and Th, respectively, (ratio of concentration in the water to the concentration in the ether).

α = observed alpha counts per minute in ether phase.

β = observed divisions per second deflection on electroscope in ether phase.

† Two successive extractions on the same sample kept separate.

‡ Pa^{233} tracer also present.

Fig. 1—Extraction of U and Th into diethyl ether from aqueous $\text{Th}(\text{NO}_3)_4$. For U and Th the values for ether phase were obtained after one extraction with an equal volume of ether. The values for ether phase were obtained after one extraction with an equal volume of ether. The values in equivalents per liter are given for $\text{Th}(\text{NO}_3)_4$ or $\text{Th}(\text{NO}_3)_4 + \text{HNO}_3$. U extraction: $\circ$, fluorescence analysis (1 to 2 mg U); $\bullet$, gravimetric analysis (50 mg U); $\bullet$, U^{232} tracer; ϕ , $R = 0.74$ in 2N HNO_3 , U^{232} tracer; ϕ , $R = 0.74$ in 6N HNO_3 , fluorescence analysis (1 mg U); $\bullet$, 2 mg U, alpha count; $\blacktriangle$, 6N HNO_3 , no Th (from the data of Kennedy and DeHaan). Th extraction: $\square$, in absence of HNO_3 ; ϕ , in presence of HNO_3 ; $\triangle$, calculated point from the data of Misciatelli.

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Paper 3.8

REMOVAL OF URANIUM FROM THORIUM BY MEANS OF A SEMICONTINUOUS SOLVENT EXTRACTOR: SOME GENERAL SOLVENT-EXTRACTION CONSIDERATIONS

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ABSTRACT

A semicontinuous solvent extractor is described, including its operating characteristics in removing small amounts of uranium from aqueous solutions of nitrate salts. Some general solvent-extraction considerations are given, involving extraction efficiencies and efficiencies in separation of two metallic species, for batch, semicontinuous, and continuous (e.g., countercurrent) extractors. The removal of about 55 mg of U^{233} from 4 kg of neutron-irradiated thorium "carbonate" by the semicontinuous method is described.

1. INTRODUCTION AND DESCRIPTION OF APPARATUS

This paper describes the preliminary considerations and experimental work involved in devising a method for the isolation of some of the first U^{233} formed by neutron irradiation of thorium in the Clinton pile according to the reaction

The material used in these studies was thorium "carbonate," a mixture of thorium basic carbonate and oxide, prepared as outlined in

Sec. 4. Also included is a summary of the processing of 4 kg of thorium carbonate for recovery of about 55 mg of U^{233} .

It appeared most feasible to remove the U^{233} from the thorium and undecayed Pa^{233} by a solvent-extraction process which could be repeated after sufficient decay of the Pa^{233} . In considering methods for carrying out this relatively small-scale separation, the possibility of using a semicontinuous extractor, similar to a design which had been used for analytical work, was investigated. [The experimental unit of Fig. 1 was designed employing as a model the analytical extractor used by N. H. Furman and coworkers.] The reasons for choosing this approach were twofold: (1) The apparatus required was relatively simple and easy to construct, and (2) it provided a convenient way of concentrating small amounts of uranium from a relatively large aqueous volume into a small volume of solvent. After a number of modifications and considerable development work, an extractor of this type was used. Figure 1 is a sketch of the design used for preliminary experimental work. Figure 2 is a somewhat simplified representation of the design finally used in isolating the U^{233} .

In operating the apparatus shown in either of the two figures, the aqueous solution from which the uranium was to be removed was placed in the extractor, and diethyl ether was placed in the distilling flask. Then, by applying heat to the distilling flask, the ether was kept boiling, condensing, and percolating through the aqueous phase as long as desired. The small apparatus, Fig. 1, was used in all preliminary studies of extraction efficiency, separation efficiency, effect of acidity, rate of flow of solvent, etc.

Diethyl ether is a convenient solvent for uranium because of its low boiling point and because of the high solubility of uranium in it. A brief description of some general solvent-extraction considerations will now be given, and then the experimental results of the U^{233} -thorium separation will be discussed.

2. EXTRACTION EFFICIENCIES AND SEPARATION EFFICIENCIES BY SOLVENT EXTRACTION

Batch, semicontinuous, and continuous (both countercurrent and perforated plate types) extractors could be used, and each has its own relative advantages, the batch being simplest but affording the lowest extraction and separation efficiencies.

2.1 Expected Extraction Efficiencies. In a batch process the distribution ratio K for a given ionic species may be expressed by the equation

$$K = \frac{C_s}{C_a} = \frac{M_s}{M_a} \times \frac{V_a}{V_s} \quad (1)$$

where C_s , M_s , and V_s represent the concentration of the extracted species, moles of the extracted species, and volume, respectively, in the solvent phase, and C_a , M_a , and V_a represent the corresponding quantities for the aqueous phase. The total original moles of solute M_o is equal to the sum of the moles in both phases after extraction, i.e.,

$$M_o = M_a + M_s$$

The fractions in the aqueous and solvent phases, respectively, after a simple batch extraction are

$$\frac{M_a}{M_o} = \frac{1}{1 + \frac{V_s}{V_a} K}$$

and

$$\frac{M_s}{M_o} = \frac{1}{1 + \frac{1}{K} \frac{V_a}{V_s}}$$

After n extractions with the same ratios V_s/V_a , assuming K is not changing (this assumption is discussed later), the fraction left in the aqueous phase becomes

$$\left(\frac{M_a}{M_o}\right)^n = \left(\frac{1}{1 + K \frac{V_s}{V_a}}\right)^n$$

Hence the required number of extractions n to reduce $(M_a/M_o)^n$ to a value a is

$$n = \frac{-\log a}{\log \left(1 + K \frac{V_s}{V_a}\right)}$$

Now to consider the semicontinuous method. This may be looked upon as a large number of batch extractions in which V_a is constant and each "single extraction" involves dV_s liters of solvent, with a

total of V_s having come in contact with the aqueous phase at the end of the process. It is assumed either that the stirring up due to the percolation of the solvent through the aqueous phase maintains C_a constant through V_a or that the advantage gained by the concentration gradient is compensated for by the disadvantage of incomplete attainment of equilibrium at the interface of the two phases. The differential equation then becomes

$$\frac{dM_s}{M_a} = \frac{dM_s}{M_o - M_s} = K \frac{dV_s}{V_a} \quad (2)$$

assuming K a constant. On integration and rearranging terms, the fraction extracted becomes

$$\frac{M_s}{M_o} = 1 - e^{-K \frac{V_s}{V_a}} \quad (3)$$

In Sec. 3 it will be seen how well this equation agrees with actual data under a few given sets of conditions.

Actually K is not a true constant under all conditions. For example, when starting with an aqueous solution of about $\frac{3}{4}M$ $\text{Th}(\text{NO}_3)_4$, $1M$ $\text{Al}(\text{NO}_3)_3$, and $1M$ HNO_3 , the nitric acid is removed relatively rapidly down to the order of $0.03M$ and then remains approximately constant over quite a wide range of V_s/V_a .¹ The value of K would be expected to fall off similarly at first, in perhaps an approximately exponential manner, and then maintain an essentially constant value over the same wide range of V_s/V_a in which the acid concentration in the aqueous phase remains constant. For such a set of conditions as these mentioned, there could be assumed for K some simple function of V_s/V_a , such as

$$K = K_0 + K_1 e^{-\alpha \frac{V_s}{V_a}}$$

where α is a constant to be determined experimentally by batch or semicontinuous extractions as are the two quantities $(K_0 + K_1)$ and K_0 .

Using this equation for K in Eq. 2, on integrating and rearranging terms, the fraction of the salt removed becomes

$$\frac{M_s}{M_o} = 1 - \left[e^{-K_0 \frac{V_s}{V_a}} \right] \left[e^{-\frac{K_1}{\alpha}} \left(1 - e^{-\frac{V_s}{V_a}} \right) \right]$$

which is a rather cumbersome equation.

In this study it was desirable to keep the pH up to about 1.0 to 1.5 in order to obtain optimum separation of U^{233} from thorium and Pa^{233} , and hence Eq. 3 was expected to hold satisfactorily at least until toward the end of the extraction.

To consider the continuous countercurrent extraction efficiency, Eq. 1 may be written

$$\frac{M_s}{M_a} = K \frac{V_s}{V_a}$$

Now if equilibrium is maintained between the two phases at the feed inlet (and no "scrub" is used), M_a at this point becomes M_o , and hence the maximum possible removal is given by

$$\frac{M_s}{M_o} = K \frac{V_s}{V_a} \quad (4)$$

This equation gives a removal efficiency that can be approached in a countercurrent column and possibly in a very tall semicontinuous extractor.

2.2 On Separation Efficiencies. In the separation of two metallic ions as uranyl and thorium by solvent extraction, certain generalizations can be made. A general graph of the fraction of each ion removed by the solvent as a function of concentration of salting agent at constant V_s/V_a ratios is expected to look like the curves in Fig. 3.

For practical reasons it is desirable to get a large fraction of the uranium removed, so a salting-agent concentration above the value a should be employed. On the other hand, in the region around c there is little increase in uranium removal and a large decrease in separation efficiency on raising the salting-agent concentration. Hence for optimum conditions a concentration around b should be selected. This is true in cases where curves shaped like those in Fig. 3 are obtained, and it is believed that the shape of these curves is fairly general. It is also believed that in going toward point c (from b), whether by increasing the salting-agent concentration or by using a "stronger" salting agent, the predictions will be the same to a first approximation. (It is of course only a first approximation, since it is very unlikely that all activities involved in the extraction mechanism will be changed by the same ratio.)

In keeping with these ideas, some data were assembled from some laboratory runs in which it was believed that the salting-out-agent concentration was in the range between b and c . A number of semi-

continuous extractions had been carried out on the 70-ml scale in which the aqueous phase contained originally 1N HNO_3 , 1N $\text{Th}(\text{NO}_3)_4$, 3N of other salting-out agent, and 1.1 mg of uranium per milliliter. The fractions of uranium and thorium removed in each successive 70-ml volume of ether were obtained and plotted against the volume of ether passed through the aqueous phase. The per cents of thorium extracted at V_s/V_a ratios where 70, 75, or 80 per cent of the uranium was extracted were obtained by interpolation using the rough curves of Fig. 3; they are presented in Table 1. Because the data were very scanty, the interpolations are far from perfect, but they are accurate enough for a qualitative comparison. The salting agents are listed in the table in order of decreasing strength, i.e., in order of decreasing efficiencies for uranium extraction at constant nitrate concentration.

The results in Table 1 are seen to be essentially in agreement with the ideas presented above; namely, that the farther one gets in the direction of c (from point b) the poorer the separation efficiency.

2.3 Concentration of Salting-out Agent for Maximum Separation Efficiency. The theoretical maximum separation efficiency depends on the shape of the curves of $\log$ (fraction extracted) vs. concentration of salting agent, at low values of the latter (in this region $\frac{M_s}{M_a} \approx$ fraction extracted). If the $\log$ curves tend to negative infinity as the concentration of salting agent approaches zero, as expected from a simple equation like

then a theoretical maximum separation efficiency does not exist at finite concentrations (i.e., greater than zero). If, however, the $\log$ curves approach constant values at low concentrations of salting agent, as indicated by work of Schuler² and Hill,³ then the theoretical maximum separation should occur at a "reasonable" concentration. The equations for determining this optimum concentration depend on the type of extraction to be employed, as will now be shown.

For a separation of uranium from thorium by a series of successive batch extractions, the desired conditions are

$$(1 - f_U)^n = \left(\frac{1}{1 + K_U} \right)^n = \text{constant} = k \quad (5)$$

where $V_s = V_a$ for each extraction; otherwise K_U must be replaced by $K_U (V_s/V_a)$.

All Th extracted $\approx nf_{Th} \approx nK_{Th} = \text{a minimum value}$

(The approximations hold if f_{Th} and K_{Th} are much less than 1. Here the f stands for the fractions extracted, and the subscripts U and Th stand for the two elements, respectively.

From Eq. 5

$$n = \frac{-\log k}{\log (1 + K_U)} = \frac{k'}{\log (1 + K_U)}$$

Hence nK_{Th} becomes

$$\frac{k' K_{Th}}{\log (1 + K_U)}$$

Now the desired value is the concentration of salting agent which makes the ratio $K_{Th}/\log (1 + K_U)$ a minimum; this value must be obtained by plotting $K_{Th}/\log (1 + K_U)$ against the concentration of salting agent.

An approximate expression can be given for the ratio $K_{Th}/\ln (1 + K_U)$, using the first two terms of the approximation (where $\ln$ stands for the natural logarithm):

$$\ln (a + x) = \ln a + 2 \left[\frac{x}{2a + x} + \frac{1}{3} \left(\frac{x}{2a + x} \right)^3 + \frac{1}{5} \left(\frac{x}{2a + x} \right)^5 + \dots \right]$$

for $a > 0$, $-a < x < \infty$

$$\frac{K_{Th}}{\ln (1 + K_U)} \approx \frac{K_{Th}}{K_U} \left(1 + \frac{K_U}{2} \right)$$

for $K_U = 0$ to $K_U \approx 3$. For semicontinuous extractions the desired conditions are

$$1 - e^{-K_U \frac{V_s}{V_a}} = \text{constant} = k \quad (6)$$

and

$$1 - e^{-K_{Th} \frac{V_s}{V_a}} = \text{a minimum},$$

i.e., $K_{Th} \frac{V_s}{V_a}$ must be a minimum. From Eq. 6

$$\frac{V_s}{V_a} = \frac{-\ln(1-k)}{K_U}$$

Hence $[-\ln(1-k)](K_{Th}/K_U)$ must be a minimum, i.e., the concentration of salting agent making K_{Th}/K_U a minimum gives the maximum separation efficiency.

In continuous or countercurrent extractions, if equilibrium is attained at the "feed" solution inlet, M_s becomes M_o in Eq. 1, and the two equations obtained are

$$\left(\frac{M_s}{M_o}\right)_U = K_U \frac{V_s}{V_a}$$

$$\left(\frac{M_s}{M_o}\right)_{Th} = K_{Th} \frac{V_s}{V_a}$$

Here again, on dividing one of these equations by the other, it is seen that the maximum separation is obtained at the salting-agent concentration where K_{Th}/K_U is a minimum.

These theoretical maxima in separation efficiency may not occur at concentration of practical value; however, merely determining whether they exist at all at "finite" concentrations of salting agent should be of definite interest to theoretical studies on the mechanism of solvent extraction.

2.4 Effect of Changing the Salting-out Agent. It is supposed that the major factors affecting efficiencies of extraction into a given solvent are the activities of various species in the aqueous phase, i.e., H^+ , NO_3^- , UO_2^{++} , or $Th(IV)$, etc., and the concentrations of the HNO_3 and/or other electrolytes in the solvent phase. It then seems reasonable to suppose that approximately the same efficiency of separation of uranium from thorium should be obtained with any salting-out agent, provided all comparisons are made under conditions of constant fraction of uranium extracted at constant V_s/V_a ratios, not at constant nitrate concentration. (The separation efficiencies will not be exactly the same, of course, since the activities of all species involved in uranium extraction and those involved in thorium extraction will probably not be exactly the same under the different conditions mentioned.) A convenient method of carrying out this comparison is to plot the per cent U and per cent Th extracted as a function of salting-agent concentration in batch extractions (keeping V_s/V_a constant) for a variety of salting agents and then to compare the values for the per

cent Th extracted at any given per cent U extracted. Unfortunately, time did not permit making such a comparison in this study.

2.5 Effect of Rate of Flow of Ether Through the Semicontinuous Extractor. Using the experimental extractor (Fig. 1), the fraction of uranium extracted by the first 70 ml of diethyl ether passing through the extractor was recorded in several different runs, each involving a different rate of flow of ether. In each case the aqueous phase originally contained 1.5M $\text{Ca}(\text{NO}_3)_2$, 0.25M $\text{Th}(\text{NO}_3)_4$, 1M HNO_3 , and 1.1 mg of U as $\text{UO}_2(\text{NO}_3)_2$ per milliliter. The results are given in Table 2.

The per cent uranium extracted at rates up to about 10 ml/min is essentially constant; above this rate the extraction efficiency begins to decrease, with the size of the ether drops passing up through the aqueous phase becoming visibly larger. For relatively small-scale work the feasible rates are quite rapid enough. The rate can be easily controlled by controlling the volume of solvent in the receiving flask, the rate increasing with increasing volume of solvent.

3. CHECK OF EQUATION 3 FOR SEMICONTINUOUS EXTRACTIONS

In order to check the validity of Eq. 3 a number of solutions were made up containing 1N HNO_3 , 1N $\text{Th}(\text{NO}_3)_4$, and 3N of an additional salting-out agent. (N here refers to molarity of nitrate ion.) Batch K's were determined for each case, using equal volumes in the two phases and diethyl ether as solvent. In two cases, i.e., those involving $\text{Al}(\text{NO}_3)_3$ and $\text{Mn}(\text{NO}_3)_2$, the K's were determined by F. W. Schuler using U^{232} tracer and a 1-ml (each phase) scale. In the cases involving $\text{Cu}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, and NH_4NO_3 , the K's were determined by chemical analysis of uranium extracted from the aqueous solutions originally containing 1 mg of uranium per milliliter; the chemical analyses were carried out by the Analytical Section under D. N. Hume using a colorimetric method.

Seventy-milliliter samples of each of these solutions containing 1 mg of UO_2^{++} per milliliter were put into a semicontinuous extractor like that shown in Fig. 1 and extracted with 70 ml of diethyl ether. After each extraction both phases were analyzed by the Analytical Section. The percentages of uranium extracted are shown in Table 3 along with the expected values from Eq. 3.

The data in Table 3 show good agreement between the calculated and experimental values for the semicontinuous extraction of uranium at a V_s/V_a ratio of unity. It is expected that the agreement would not be good for higher V_s/V_a ratios, if the values of K given in Table 1 were used, since the true K's should decrease with increasing V_s/V_a because of the removal of HNO_3 . If, however, the original aqueous

solution had a pH of about 1.5, then the pH would not be expected to change appreciably with V_s/V_a and hence neither should K (see Sec. 2).

4. EXTRACTION OF U^{233} FROM IRRADIATED THORIUM CARBONATE

The type of extraction apparatus used in the U^{233} -thorium separation was essentially like that shown in Fig. 2 except for a few modifications, the most important of which was the addition of an automatic siphon between the extractor and receiving flask to measure the flow rate of the solvent. An outline of the procedure employed for the U^{233} -thorium separation and a brief discussion of the various steps follow. The process involved

1. Dissolution of the irradiated thorium carbonate in HNO_3 .
2. A first semicontinuous solvent extraction after adjustment of concentrations and pH.
3. Removal of the U^{233} with all extracted $Th(NO_3)_4$ from the receiving flask and putting it through a second semicontinuous extraction.
4. Removal of the U^{233} with all extracted $Th(NO_3)_4$ from the extraction receiving flask and precipitation of the thorium as the oxalate away from the uranium at 1N HNO_3 .
5. Neutralization of this supernatant to pH 7.0 with NH_4OH and electroplating the U^{233} onto a platinum cathode from the resulting $(NH_4)_2C_2O_4 - NH_4NO_3$ solution.
6. Dissolving the U^{233} off the platinum cathode with dilute HNO_3 .

The thorium carbonate used in these experiments was purchased from Lindsay Light & Chemical Co., West Chicago, Ill., as the basic carbonate, $ThOCO_3 \cdot 2H_2O$, and heated at $250^\circ C$ to remove water vapor and easily removable gases. After this treatment the resulting material could be represented as about 90 to 95 per cent ThO_2 and about 10 to 5 per cent partly hydrated $ThOCO_3$. Fortunately this material, unlike pure ThO_2 , is soluble in HNO_3 . This thorium carbonate for irradiation in the Clinton pile was compressed into pellets and sealed in aluminum cans (the same type cans as used for Clinton uranium metal slugs), each can containing 200 g of the thorium "compound."

It was decided to dissolve the can along with the thorium carbonate and use the resulting aluminum nitrate as an additional salting-out agent, rather than to first dissolve the cans in $NaOH$ and then the carbonate in HNO_3 , after removing the sodium aluminate solution. In order to be able to adjust the final HNO_3 concentration more closely, the dissolution was carried out in two steps. First, the aluminum was

dissolved in excess 3.5N HNO_3 containing 0.004N $\text{Hg}(\text{NO}_3)_2$ as a catalyst, after which the excess HNO_3 was boiled off. Then the carbonate was dissolved in sufficient 14N HNO_3 , at the boiling point, to end up with a solution containing roughly 0.95 mole of $\text{Th}(\text{NO}_3)_4$ to 0.73 mole of $\text{Al}(\text{NO}_3)_3$ to 1 mole of HNO_3 . This solution was then adjusted to a pH of about 1.5 with NH_4OH , and the total concentration was diluted to 7.0N (i.e., 7.0M NO_3^-) and sent to a storage tank. From the tank the solution went by gravity flow to the first semicontinuous extractor in 1.1-liter batches. (Dilution to 5M total nitrate was found to give a higher separation efficiency; however, it required a longer extraction time, and the increased separation was not appreciably advantageous to the over-all process.) Both the dissolver and storage tank were made of 25-12 stainless steel, the extractor, of glass.

The cans which were processed by the method described here had been irradiated in the Clinton pile as follows:

1. Fourteen cans had been irradiated for $4\frac{1}{2}$ months in a position where the flux was somewhat less than average; then they had been allowed to stand for about two months before processing. Each of these slugs at the time of processing contained about 2.5 mg of U^{233} and 0.2 mg of Pa^{233} .

2. Six cans had been irradiated for about five months in a position where the flux was nearer its maximum value; then they were processed within about 10 days after removal from the pile. Each can contained at the time of processing about 4 mg of U^{233} and 1.5 mg of Pa^{233} .

Because of the beta and gamma radiation associated with the Pa^{233} , i.e., 20 curies of 0.23-Mev betas and about 10 curies of 0.33-Mev gammas per milligram, the process through the first solvent-extraction step had to be carried out behind a few inches of lead shielding. After the first semicontinuous extraction, the remaining steps were carried out essentially without shielding.

During the first extraction the receiving flask contained about 100 ml of aqueous phase and about 100 ml of diethyl ether, the water being present to remove any extracted HNO_3 from the ether in order to avoid the possibility of a violent reaction involving the solvent and this acid. After percolating ether through the aqueous phase in the extractor equivalent to six volumes of the latter (i.e., 6.6 liters passing through), a stopcock was turned, and the 100 ml of ether was boiled away from the aqueous phase in the boiler. Some oil was left on top of the water layer, and it was extracted off with benzene. The oil may have come from the dissolver or storage tank (although these had been thoroughly rinsed with carbon tetrachloride and concentrated nitric acid), or it may have resulted from nitrate reaction with the

ether during the extraction. There were reducing agents remaining in the aqueous phase which had been found on test to interfere with the second extraction. These were destroyed by titration with potassium permanganate.

Several "extracts" from the first extraction were combined and after making 7N (3.5M) with respect to $\text{Ca}(\text{NO}_3)_2$ were put through the second semicontinuous extraction. Ether was percolated through the aqueous phase until an equivalent of four times the aqueous volume had passed through. The extracted U^{233} was again collected in an aqueous phase as in the first extraction. The losses in each of the two extractions were in the range of about 1 to 3 per cent.

At this point the U^{233} had a few times its weight of thorium remaining with it, showing a removal of thorium by a factor of up to about 10,000. After again destroying the reducing agents with potassium permanganate, the solution was made 0.5N in HNO_3 , and the thorium was precipitated away with excess oxalic acid. Above 0.5M HNO_3 the precipitation of thorium is less complete; below about 0.5M HNO_3 the precipitate begins to carry more uranium and has poorer physical properties for handling. It was found that the thorium could be precipitated at concentrations of up to 55 mg/ml without losing more than about 1 per cent of the U^{233} into the precipitate.

After removal of the thorium oxalate precipitate the solution was adjusted to pH 7.0 with NH_4OH , and the U^{233} was electroplated onto a platinum cathode at 80°C , using conditions similar to those recommended by Cohen and Hull,⁴ with the exception that appreciable ammonium nitrate was present in these runs. The U^{233} was then dissolved off the platinum with dilute HNO_3 solution. Part of the product was further purified by additional batch extractions; after this treatment the metallic impurities were present to an extent of probably less than 1 per cent.

Table 1—Per Cent Thorium Extracted (by the Semicontinuous Method) into Diethyl Ether from Aqueous Solutions Containing 1N HNO_3 , 1M $\text{Th}(\text{NO}_3)_4$, 3N of the Salting Agent Shown, and 1.1 Mg of Uranium per Milliliter

Salting agent	70% U extracted		75% U extracted		80% U extracted	
	V_s/V_a	% Th extracted	V_s/V_a	% Th extracted	V_s/V_a	% Th extracted
$\text{Al}(\text{NO}_3)_3$					1.0	0.60
$\text{Mn}(\text{NO}_3)_2$	0.7	0.30	1.0	0.35	1.3	0.39
$\left. \begin{array}{l} 0.75\text{N } \text{Al}(\text{NO}_3)_3 \\ 2.25\text{N } \text{Ca}(\text{NO}_3)_2 \end{array} \right\}$	1.1	0.15	1.3	0.17	1.6	0.17
$\text{Ca}(\text{NO}_3)_2$	1.7	0.10	2.0	0.11	2.4	0.12
NH_4NO_3	5.0*	0.08*				

*Extrapolated values.

Table 2—Per Cent U Extracted as a Function of Ether Flow Rate

Ether throughput		% U extracted in first 70 ml of ether
Min/70 ml of ether	ml/min	
6.6	10.6	52.5
11.0	6.36	56.3
12.0	5.83	56.0
24.8	2.82	57.1

Table 3—Experimental and Calculated Values for Semicontinuous Extraction of Uranium into Diethyl Ether from Aqueous Solutions 1N in HNO_3 , 1N in $\text{Th}(\text{NO}_3)_4$, and 3N in Salting-out Agent at a V_s/V_a Ratio of Unity

Salting-out agent	Batch extraction		% U extracted by semi-continuous extraction	
	% extracted	$K = C_s/C_a$	Calculated	Experimental
$\text{Al}(\text{NO}_3)_3$	67	2.0	86	82
$\text{Mn}(\text{NO}_3)_2$	55	1.2	70	74
$\text{Cu}(\text{NO}_3)_2$	55	1.2	70	71
$\text{Ca}(\text{NO}_3)_2$	40	0.66	48	55
NH_4NO_3	19	0.24	21	22

Fig. 1 — Experimental semicontinuous extractor. (1) Condenser. (2) Aqueous-ether interface (2-cm-diameter tubing). (3) Extractor (3-cm-diameter tubing; 70 ml aqueous phase). (4) Sintered-glass disk (coarse). (5) Receiving flask. (6) Constant-temperature water bath. (7) Hot-plate. (8) Three-way stopcock (for discharging aqueous solution).

Fig. 2—Semicontinuous extractor used in the separation of U^{233} from thorium. (1) Condenser. (2) Aqueous inlet. (3) Aqueous outlet (to waste). (4) Extractor (1.1 liter aqueous capacity). (5) Receiving flask. (6) Constant-temperature water bath. (7) Sintered-glass disk (coarse). (8) Hot plate.

Fig. 3—General graph of the fraction of each ion removed by the solvent as a function of concentration of salting agent.

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Paper 3.10

THEORETICAL CONSIDERATION OF ETHER EXTRACTION
OF URANYL NITRATE FROM AQUEOUS SOLUTIONS CONTAINING
VARIOUS METAL NITRATE SALTING AGENTS

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ABSTRACT

It is pointed out that the extraction of uranyl nitrate from aqueous solution by immiscible solvents such as diethyl ether is probably accompanied by a change in solvation. A quantitative theory of the extraction mechanism is developed in which the effects of solvation are included. Comparison is made between the theory and currently available data.

1. INTRODUCTION

Many water-immiscible organic liquids such as alcohols, ethers, esters, and ketones dissolve uranyl nitrate and act to extract it from aqueous solutions.¹ The distribution coefficient is a function of the concentration of uranyl nitrate² and can be improved by the addition of other nitrates to the aqueous phase.^{3,4} Although much empirical information has been gathered on distribution coefficients between specific organic and water phases, no adequate theory for the solvent extraction of uranyl nitrate has been developed by which these data may be correlated or extended. This situation results from the condition that, despite its experimental simplicity, the solvent extraction of an inorganic salt from concentrated salt solutions is a theoretically complex process and the actual chemistry involved has not been deter-

mined. It is the purpose of this paper to propose a chemical mechanism for the diethyl ether extraction of uranyl nitrate and to test this mechanism in a quantitative analysis of certain data pertaining to the system.

The uranyl nitrate-diethyl ether system was chosen for study because the solubility of uranyl nitrate in diethyl ether has long been known and this system is probably the best known solvent-uranyl nitrate system available. The suitability of the proposed extraction mechanism will be judged by the ability of a derived thermodynamic function to reproduce quantitatively the experimental data on the extraction of uranyl nitrate by diethyl ether. In order to simplify the application of known thermodynamic solution data, we will consider the extraction of uranyl nitrate from solutions sufficiently acid to avoid hydrolysis, and also free of interfering ions.

2. PROPERTIES OF URANYL NITRATE IN SOLUTION

In order to formulate a reasonable uranium-extraction mechanism which is consistent with the chemical nature of uranyl nitrate, the following properties exhibited by uranyl nitrate in aqueous solutions and in solvent extraction must be borne in mind. Uranyl nitrate is a strong electrolyte, acting as if it were completely dissociated in water. Robinson, Wilson, and Ayling,⁵ from their studies of the activity coefficients of bivalent metal nitrates, concluded that it was unlikely that there was any intermediate ion formation for uranyl nitrate. Uranyl, magnesium, cobalt, copper, cadmium, calcium, strontium, and barium nitrates were studied; at any concentration the mean-activity coefficient of uranyl nitrate was consistently the highest. Therefore, even when uranyl nitrate is present in low concentration in strong nitrate solutions, it might be expected that the uranium exists largely as uranyl ion.

Although the solubility of uranyl nitrate is appreciable in anhydrous ether, it rises rapidly with the addition of water to the system.² Thus the ether phase in equilibrium with anhydrous $\text{UO}_2(\text{NO}_3)_2$ contains 8.78 per cent by weight of uranyl nitrate at 20°C, whereas ether in equilibrium with crystalline $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and a saturated water layer contains 45.27 per cent by weight of uranyl nitrate. The ether phase in the latter case also contains 13.56 per cent by weight of water, as compared to normal solubility of water in ether of 1.3 per cent by weight. The enhanced solubility of water in ether, despite the decreased activity of water in the highly concentrated aqueous phase, along with the increased uranyl nitrate solubility in ether in the presence of water, suggests that the uranium extracted from an aqueous into an ether phase may be both ether and water solvated. This hy-

pothesis is substantiated by the composition of the compounds obtained on the evaporation of an ethereal solution of uranyl nitrate hexahydrate. Von Unruh,⁶ on evaporating such a solution in vacuum or dry air, obtained fluorescent yellow-green crystals whose composition was $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{C}_4\text{H}_{10}\text{O}$. Further evidence as to the nature of the uranyl nitrate in ether comes from the observation that, when an excess of crystalline uranyl nitrate hexahydrate is shaken with ether, two liquid layers are formed and an elevation of temperature is noted.⁷ This is indicative that the uranyl ion is associated with less than six molecules of water in concentrated ether solution. The attachment of both water and solvent to the uranium in the solvent phase necessitates consideration of water and ether as components in the extraction reaction, and, since the change in the number of molecules of water associated with each extracted uranium molecule may be large, relatively small changes in the water activity may be amplified through a power relationship to a large effect on the extraction equilibrium.

The addition of nitric acid decreases the solubility of uranyl nitrate in water and changes the hydrate in equilibrium with the solution.⁸ The solubility of uranyl nitrate as a function of nitric acid concentration shows points of discontinuity, the solubility reaching a minimum and then rising for each lower hydrate with which it can be brought into equilibrium. The changing degree of hydration of the equilibrium solid phase may be indicative of a changing degree of hydration of the uranyl ion in the aqueous phase. If it is assumed that water enters into the solvent-extraction reactions, then changing degrees of hydration may change the power relationship with which water activities enter into calculations at different solution salt concentrations, greatly complicating the analysis. In the practical case, however, solutions of water activity as low as 0.45 are not used, so this problem need not be considered further.

3. MECHANISM OF ETHER EXTRACTION

We assume a mechanism for the ether extraction of uranyl nitrate which involves a competition of water and ether for uranyl nitrate. In the aqueous phase the following pertinent reactions are postulated:

$[\text{UO}_2^{++}]$ will be designated by U; $[\text{NO}_3^-]$ will be designated by N; H_2O will be designated by H; ether will be designated by E; activities will be

designated by a ; molalities will be designated by m ; forms present in the ether will be designated by primes. The hydrolysis reaction for uranyl ion is neglected in these considerations because at acidities above 0.1N it removes an inappreciable portion of the uranium from the solvent-extraction reactions.]

The following equilibrium constants can be written:

$$K_1 = \frac{a_{(UN_2)(xH)}}{a_{U(xH)} a_N^2} \quad (3)$$

$$K_2 = \frac{a_{(UN_2)(zH)(yE)} a_H^{(x-z)}}{a_{(UN_2)(xH)} a_E^y} \quad (4)$$

It is further assumed that $(UN_2)(yE)(zH)$ has a distribution markedly in favor of the ether (experimental distribution coefficients greater than 100 have been found) and that the other forms of uranium are essentially not extractable. The ratio of concentrations of uranium in the water and ether phases following equilibration may then be represented by

$$R = \frac{m_{(UN_2)(zH)(yE)} + m_{(UN_2)(xH)} + m_{U(xH)}}{m'_{(UN_2)(zH)(yE)}} \quad (5)$$

with the equilibrium condition being

$$(m\gamma)_{(UN_2)(zH)(yE)} = (m'\gamma')_{(UN_2)(zH)(yE)} \quad (6)$$

Algebraic combination of Eqs. 3 to 6 leads to the equation

$$R = \left(\frac{\gamma'}{\gamma} \right)_{(UN_2)(zH)(yE)} + \frac{\gamma'_{(UN_2)(zH)(yE)} a_H^{(x-z)}}{K_2 a_E^y \gamma_{(UN_2)(xH)}} \left[1 + \frac{m_{U(xH)}}{m_{(UN_2)(xH)}} \right] \quad (7)$$

4. EVALUATION OF PROPOSED MECHANISM

In testing the suitability of the derived equation, a number of approximations must be made to evaluate quantities which are difficult or impossible to compute from the presently available data. Since corrections to some of these details may be possible later when more data are available, it is worth while to proceed with such an evaluation with a clear understanding of the limitations involved.

The experimental data on distribution of uranyl nitrate between aqueous and ether phases come from a study by Hellman and Wolf⁴ (Table 1). Their experiments consisted in putting radioactive trace amounts of uranium as uranyl nitrate in solutions of a bulk nitrate salt (concentrations from 1N to 10N), 0.5N in nitric acid, equilibrating with an equal volume of diethyl ether, and determining the fraction of the radioactive tracer extracted by the ether. The extraction of bulk salt was in most cases undetectable, although extreme concentrations of cupric nitrate did give traces extracting. Since the experiments cited concerned only trace concentrations of uranyl nitrate and inappreciable amounts of the bulk salt extracted, the important factors affecting the activity of the ether in the ether phase should be the amount of water dissolved and the amount of nitric acid extracted. With pure ether and water alone, about 1.3 per cent by weight of water dissolves in ether, amounting to perhaps 5.1 mole per cent. Addition of salt to the water phase in equilibrium with the ether decreases the vapor pressure of the water and its concentration in the ether phase. The originally low extraction of nitric acid increases as salt concentration increases, but it never approaches the 5 mole per cent of water. It seems legitimate therefore, within the accuracy of the experimental data involved, to consider the activity of the ether in the system as essentially constant.

If one further makes the explicit assumption that the formula of the extracted hydrate-etherate is trihydrate-monoetherate, in conformity with some of the earlier cited data on the compounds crystallized from ether, and that in the aqueous phase the uranium is closely coordinated with only six molecules of water, the activity of the ether may be taken as constant (and unity), and the activity coefficient of the water, appearing in the same term of Eq. 7, will then be raised to the power 6 minus 3, or 3. Furthermore, since the hydrate-etherate appears to only trace concentrations in essentially pure ether, its solution may be considered to be ideal, and its activity coefficient therefore constant in that medium.

The activity of water in a given salt solution, in the form of the partial pressure of water above the solutions in question, can be obtained from the literature; by convention the activity is taken as the ratio of the partial pressure to the vapor pressure of pure water at the same temperature.

The ratio of ionic uranyl to that in the form of uranyl nitrate is difficult to obtain directly. The choice must be made first as to whether to consider the salt a weak or strong electrolyte. If it is a weak electrolyte, under the experimental conditions outlined (trace concentrations of uranyl nitrate in high concentrations of bulk nitrate),

one would expect it to be largely in the form of the undissociated salt. Under such circumstances the ratio in question becomes very small, and the last, bracketed term in Eq. 7 reduces to unity. In the alternative case of a strong electrolyte which is largely dissociated at all nitrate concentrations, apparently "undissociated" molecules will be related in frequency of appearance to the statistical juxtaposition of a uranyl ion and two nitrate ions. The value of the ratio of ionic to molecular form should then be a function of the inverse square of the nitrate ion activity, and the term in brackets may then be reduced to the second portion alone, most of the uranium being in the ionic form.

The practical expedient was adopted of calculating the two extreme cases of no dissociation and essentially complete dissociation. For the latter case, as outlined, the activity coefficient of the undissociated molecule cancels out, leaving the ionic-activity coefficient product in the denominator. To evaluate the coefficient product, the assumption is made that it is equal to the cube of the mean-activity coefficient of uranyl nitrate. Examination of data compiled by Harned and Owen⁹ on the behavior of HCl in bulk chloride solutions indicates that, to a good approximation, the mean-activity coefficient of trace concentrations of an electrolyte in a bulk salt solution of given ionic strength is equal to the geometric mean of the mean-activity coefficient of the bulk salt and that of the trace electrolyte present alone at the same ionic strength. Illustration of how this rule approximates the trace mean-activity coefficient is shown in Table 2, calculated from data given by Harned and Owen. Data given in this same work indicate that in concentrated salt solutions the activity coefficients of minor constituents are essentially constant where their concentration is less than 0.01 to 0.1 molal. Accordingly, this geometric mean relationship has been used to obtain mean-activity coefficients for trace uranyl nitrate. Mean-activity-coefficient values were extrapolated from a graph of $\log \gamma_{\pm}$ against ionic strength (Fig. 1). [Activity coefficients for lithium, calcium, magnesium, copper, and uranyl nitrates were taken from Robinson and coworkers;^{5,10} aluminum nitrate, from Pearce.¹¹ Nitric acid to 3M was taken from Lewis and Randall,¹² values for higher concentration being calculated from partial pressure of water (International Critical Tables data). Manganous nitrate activity coefficients were obtained from water partial-pressure data of Ewing, Glick, and Rasmussen,¹³ using the KCl data of Robinson and Sinclair,¹⁴ and Harned et al.⁹ to determine a base line value at 1.14 molal. Ammonium nitrate data were similarly calculated from solvent partial-pressure data of Gibson and Adams¹⁵ at 20.3°C, without attempting correction to 25°C. Water-activity data not directly obtained were calculated

from the data of Robinson et al.^{5,10,14]} Values are given in Table 3. A graph of $\log R$ against $\log (a_H/\gamma_{\pm})^3(1/m_N)^2$ is given in Fig. 2.

For evaluation of the activity coefficient of the undissociated uranyl nitrate, in considering the case of uranyl nitrate as a weak electrolyte, it is helpful to rearrange Eq. 3 into the following form:

$$\gamma_{(UN_2)(xH)} = K_1 \left[\frac{m_U m_N^2}{m_{(UN_2)(xH)}} \right] \gamma_U \gamma_N^2 \quad (8)$$

As a first approximation one might take the activity coefficient of the undissociated molecule as unity, since salt effects on neutral molecules are in general not large. The second term of Eq. 7 thus becomes reduced to a function of the cube of the water activity which obviously fails to describe the data. Another sort of approximation may be made, namely, that the molality function in brackets, Eq. 8, is constant. This amounts to saying that a reasonably good "dissociation constant" is obtained from considering the molalities without recourse to activities. In this case the ionic-activity product is reduced to the cube of the mean-activity coefficient, as was done above. A graph of the data on this basis is shown in Fig. 3.

The problem of the activity coefficient of the neutral uranyl nitrate can also be approached from the conventional direction of salting-out of neutral molecules, for which the following approximate relation often holds:⁹

$$\log \gamma = k\mu \quad (9)$$

The quantity μ is the ionic strength, and k is a constant, different for each salt and each neutral molecule. To substitute a value for k is not practical, since there is no criterion for predicting values. It is therefore necessary to ignore the factor of the activity of the water and to plot logarithm of R against ionic strength. The graph is shown in Fig. 4.

5. DISCUSSION

From consideration of Eq. 7 it is seen that a graph of the logarithm of R against the logarithm of the function $\log (a_H/\gamma_{\pm})^3(1/m_N)^2$ should give a straight line at an angle of 45 deg if the neglected terms are really negligible. If they are not, the graphs should be flattened correspondingly. Figure 2 shows a scattering, but individual salt lines show a straight-line tendency. The slopes are all less than 45 deg. In spite of the scatter, the lines for lithium, copper, magnesium, and manganous nitrates show very good agreement, with an essentially uniform slope

and position, the spread of the group being less than a factor of 1.5 in R over a considerable range of R . Considering the errors inherent in the data and in terms which are the cube of extrapolated values, the concurrence of the results is striking. The behavior of nitric acid is actually in agreement with that of the four salts mentioned above, since it is known that nitric acid extracts into ether and no correction has been applied to either the water concentration of nitric acid or the ether activity. As expected, the nitric acid point at low concentration of acid, where these corrections would be least, falls in the range of the four salts showing agreement. Distinct disagreement with the trend of these five nitrates is shown in the case of ammonium nitrate, which shows a slightly flatter slope, lying a factor of 3 in R above the main group, and calcium and aluminum nitrates, which lie below the main group. Even these, it should be reiterated, show slopes not exceeding 45 deg. A possible explanation for the deviations will be mentioned below.

As in the case of Fig. 2, Fig. 3 should show a line at 45 deg, or, if neglected quantities interfere, a flatter line. In addition to the rather more evident kinks in individual lines, there is an evident lesser uniformity of slope. Several lines, such as those for calcium and magnesium nitrates, and in the early region, lithium nitrate, show slopes definitely steeper than the limiting 45 deg. In the lower concentration region, both nitric acid and ammonium nitrate become grouped with the majority concentration, but magnesium and lithium nitrates become distinct deviates. Aluminum and calcium are still far from the norm. In our estimation Fig. 2 gives a cleaner and less questionable approximation to the theoretical requirements than Fig. 3, lending support both to the strong electrolyte nature of uranyl nitrate and the relationship deduced (Eq. 7) for the extraction of uranyl nitrate by ether.

It will be pointed out, of course, that Fig. 4, which is another representation of the hypothesis that uranyl nitrate is a weak electrolyte, does give an appearance similar to that generally reported for salting-out studies—a family of lines, with slopes dependent on the salt used, relating the logarithm of the activity coefficient of the neutral molecule and the ionic strength of the salt solution.⁹ However, this graph does not necessarily furnish evidence for the status of uranyl nitrate as a weak electrolyte. This is seen upon analyzing the factors which enter into evaluation of Eq. 7, as plotted in Fig. 2. The activity of the water in the salt solution is a function (although not precisely logarithmic) of the ionic strength; the mean-activity coefficient for uranyl nitrate is taken from a graph (Fig. 1) which itself shows a logarithmic relationship of activity coefficient and ionic strength; the

nitrate concentration is proportional to the ionic strength; and these factors all come in as squares and cubes. It is therefore clear that obtaining curves crudely of the type expected from ionic-strength graphs can be no real criterion of the weak electrolyte nature of uranyl nitrate.

Inspection of Fig. 1 shows further that of the salts used, in the high-ionic-strength region, all give reasonably straight-line extrapolations with positive slope except ammonium nitrate. This salt gives an almost straight-line salting-in graph. It is possible that the ammonium nitrate-extraction line of Fig. 2 lies above the general group because the hydrate-etherate is salted in instead of out. The tendency of calcium and aluminum nitrates to fall below the main group could be due to unusually powerful salting-out action on the hydrate-etherate, but this seems less likely.

It therefore appears that the hypotheses and calculations leading to and embodied in Eq. 7 are compatible with the evidence available on the extraction of uranyl nitrate by organic liquids. The hypothesis further gives qualitative explanation of phenomena such as the decrease of extraction of the uranyl nitrate when high enough concentrations of copper nitrate and thorium nitrate are used to extract appreciably into the ether phase.⁴ The effect is due to lowering of the ether activity and also changing the activity coefficient of the uranyl nitrate extracted into it. A more exact evaluation of the relations derived must await very careful experiments designed specifically to yield a quantitative test of Eq. 7.

6. SUMMARY

On the hypotheses of (a) strong electrolyte behavior of uranyl nitrate, (b) reaction of ether with hydrated uranyl nitrate to give a compound containing one molecule of ether with loss of three waters, and (c) extraction of the resulting hydrate-etherate into the organic phase, an equation has been derived for the distribution of uranyl nitrate between water and ether. Test of the relationship has been made with data available for the extraction of trace concentrations of uranyl nitrate from strong salt solutions. Within the limits of accuracy of the data used, the relationship shows distinct promise.

Table 1—Extraction of Trace Uranyl Nitrate from Salt Solutions 0.5N in Nitric Acid by Equal Volumes of Diethyl Ether (Hellman and Wolf, 1945)

Agent	Normality	Per cent extracted	Agent	Normality	Per cent extracted
HNO ₃	3	23	Mg(NO ₃) ₂	1.5	3
	5	52		2.6	18
	7	62		3.6	38
LiNO ₃	2	10		5.5	99
	3.5	36	Mn(NO ₃) ₂	2.5	18
	5.5	74		5.0	74
	7.5	81		7.5	87
NH ₄ NO ₃	3	8	Cu(NO ₃) ₂	2.5	12
	5.5	25		5.0	69
	10	59		7.5	91
Ca(NO ₃) ₂	2.4	13		10.5	87
	3.6	32	Al(NO ₃) ₃	2.0	18
	4.9	63		4.0	54
	7.5	99		6.0	96

Table 2—Calculation of Mean-activity Coefficient for Trace Concentrations of a Salt in the Presence of a Bulk Salt

Bulk salt	$\gamma_{\pm}$ of HCl* ($\mu = 3$)	$\gamma_{\pm}$ of bulk salt ($\mu = 3$)	$\gamma_{\pm}$ of HCl (0.01M)	$\gamma_{\pm}$ calc.†
LiCl	1.32	1.17	1.29	1.24
NaCl	1.32	0.72	1.07	0.97
KCl	1.32	0.58	0.84	0.87
CsCl	1.32	0.48	0.67	0.79
SrCl ₂	1.32	0.46	0.88	0.78
BaCl ₂	1.32	0.39	0.72	0.72
AlCl ₃	1.32	0.38	0.85	0.71
CeCl ₃	1.32	0.34	0.70	0.67

*Data taken from Harned and Owen.

†Calculated by formula $\gamma_{\pm} = \sqrt{(\gamma_{\pm} \text{ HCl}) (\gamma_{\pm} \text{ bulk salt})}$.

Table 3—Calculation of Uranyl Nitrate Distribution Functions

Salt	Normality	NO ₃ ion molality	Ionic strength	Mean-activity coefficient			Water activity	(a/γ±)	(a/γ) ³ × 10 ³	(a/γ) ³ N ² × 10 ³	a ³	R
				Bulk salt	Bulk UO ₂ (NO ₃) ₂	Trace UO ₂ (NO ₃) ₂						
HNO ₃	3	3.3	3.3	0.92	0.812	0.864	0.894	1.035	1,100	101	0.714	2.64
	5	5.9	5.9	1.14	1.138	1.255	0.784	0.625	244	7.0	0.482	0.77
	7	9.0	9.0	1.39	2.67	1.93	0.667	0.346	41.4	0.51	0.297	0.56
NH ₄ NO ₃	3	3.3	3.3	0.402	0.812	0.660	0.916	1.604	4,100	376	0.769	9.7
	5.5	7.6	7.6	0.285	1.98	0.571	0.837	1.114	1,370	23.7	0.586	3.0
	10	>15	>15	0.2	10	1.4	<0.73	0.52	140	0.62	0.39	1.0
LiNO ₃	2	2.15	2.15	0.862	0.660	0.754	0.918	1.218	1,810	392	0.774	6.8
	3.5	3.9	3.9	1.12	0.912	1.01	0.838	0.830	572	37.6	0.588	1.42
	5.5	6.6	6.6	1.68	1.60	1.64	0.698	0.426	77.3	1.77	0.340	0.30
	7.5	9.75	9.75	2.70	3.17	2.93	0.559	0.191	7.0	0.074	0.175	0.21
Ca(NO ₃) ₂	2.4	2.5	3.75	0.333	0.885	0.543	0.942	1.73	5,180	829	0.836	5.0
	3.6	3.95	6.0	0.343	1.40	0.693	0.903	1.30	2,200	141	0.736	1.68
	4.9	5.55	8.25	0.368	2.28	0.916	0.658	0.937	823	26.7	0.632	0.48
	7.5	9.5	14.25	0.50	8.5	2.06	0.70	0.34	39	0.43	0.343	0.01
Mg(NO ₃) ₂	1.4	1.55	2.3	0.518	0.678	0.592	0.958	1.62	4,250	1770	0.879	24
	2.6	2.75	4.1	0.648	0.950	0.784	0.912	1.16	1,560	206	0.759	3.45
	3.6	3.9	5.9	0.861	1.38	1.09	0.861	0.790	493	32.4	0.638	1.26
	5.5	6.4	9.6	1.71	3.05	2.28	0.745	0.327	35.0	0.85	0.413	0.01
Cu(NO ₃) ₂	2.5	2.65	4.0	0.505	0.928	0.684	0.924	1.35	2,460	350	0.789	5.5
	5.0	5.7	8.6	0.831	2.46	1.43	0.805	0.563	178	5.5	0.522	0.36
	7.5	9.4	14.1	1.6	8.4	3.66	0.65	0.178	5.6	0.063	0.275	0.09
Mn(NO ₃) ₂	2.5	2.65	3.98	0.592	0.925	0.740	0.923	2.63	18,200	4550	0.871	3.35
	5.0	5.70	8.55	0.995	2.42	1.55	0.801	1.12	1,400	75.7	0.652	0.65
	7.5	9.35	14.0	2.48	8.2	4.51	0.625	0.359	46.3	0.97	0.392	0.034
Al(NO ₃) ₃	2.0	2.0	4.0	0.142	0.928	0.363	0.955	1.25	1,953	278	0.786	3.51
	4.0	4.3	8.6	0.243	2.46	0.773	0.867	0.5168	138	4.25	0.514	0.29
	6.0	6.9	13.8	0.535	7.8	2.04	0.732	0.1386	2.65	0.03	0.244	0.13

Fig. 1—Logarithm of mean-activity coefficient against ionic strength for various nitrates. H, nitric acid; Li, lithium nitrate; NH₄, ammonium nitrate; Ca, calcium nitrate; Mg, magnesium nitrate; Cu, cupric nitrate; UO₂, uranyl nitrate; Al, aluminum nitrate; Mn, manganous nitrate. For sources of data, see text.

Fig. 2—Logarithm of distribution coefficient, water/ether, of trace uranyl nitrate between various nitrate salt solutions and diethyl ether, against logarithm of the product: (water activity)³ (mean-activity coefficient, uranyl nitrate)⁻³ (nitrate ion molality)⁻².

Fig. 3—Logarithm of distribution coefficient, water/ether, of trace uranyl nitrate between various nitrate salt solutions and diethyl ether, against logarithm of the product. (water activity)³ (mean-activity coefficient, uranyl nitrate)⁻³

Fig. 4—Logarithm of distribution coefficient, water/ether, of trace uranyl nitrate between various nitrate salt solutions and diethyl ether, against ionic strength of the salt solution.

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Paper 3.11

INFLUENCE OF VARIOUS NITRATES ON DIETHYL
ETHER EXTRACTION OF LOW CONCENTRATIONS OF
URANIUM FROM THORIUM

By Nison N. Hellman and Michael J. Wolf

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1. INTRODUCTION

The production of U^{233} by neutron irradiation of thorium^{1, 2} presents the problem of isolating and purifying uranium from thorium when present at concentrations less than one ten-thousandth that of thorium. The known solubility of uranyl nitrate in diethyl ether suggested the possibility of using a solvent-extraction process, and preliminary work by Fontana³ proved the feasibility of such an extraction and purification procedure.

Upon shaking an aqueous solution of uranyl nitrate with ether, the uranyl nitrate distributes itself between the aqueous and ether phases. The completeness of extraction which occurs in a single equilibration of ether and aqueous phases is generally controlled by varying the concentration of a nitrate salt in the aqueous solution, the extraction being low in dilute solutions and reaching a maximum in more concentrated solutions. In connection with the development of a solvent process for extraction of U^{233} which was undertaken in this laboratory,⁴ studies were made of the influence of various nitrates on the extraction of thorium and uranium into ether. It was the purpose of these studies to determine the most favorable salting agent and the optimum concentration of that agent to achieve separation of uranium from thorium. The influence of HNO_3 , NH_4NO_3 , $LiNO_3$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $Cu(NO_3)_2$, $Mn(NO_3)_2$, $La(NO_3)_3$, $Al(NO_3)_3$, and $Th(NO_3)_4$ at various concentrations was determined (Table 1 and Figs. 1 to 10).

2. EXPERIMENTAL WORK

The experimental methods for this investigation were the same as those employed by Hyde and Wolf⁵ for a survey of solvents for extraction of U^{233} . The procedure consisted in shaking 5 ml of ether with 5 ml of aqueous phase of appropriate composition with respect to salting agent, thorium, and U^{233} tracer. This was done in a glass-stoppered 15-ml centrifuge cone. After 10 min of shaking, the tubes were centrifuged to effect a clear separation of the layers. A 2-ml aliquot was then taken from the ether layer; the ether was evaporated over water; and the resulting aqueous solution was analyzed for thorium and uranium. The thorium analyses were performed by the precipitation of the oxalate by oxalic acid in 1N hydrochloric acid and the subsequent oxidimetric determination of the oxalate by titration with ceric sulfate. Uranium analyses were made by measuring the alpha activity of the extracted U^{233} . Five to eight thousand counts per minute of tracer (52 per cent counting yield) were used in each experiment. It was found that the variation in the amount of tracer from 100 to 100,000 c/min in 5-ml volume did not change the percentage extraction. In those studies where thorium was present (except those in which thorium nitrate served as a salting agent) its concentration was held at 1N. Nitric acid was present in 0.5N concentration in all experiments.

All the salts tested were able to induce uranium of better than 60 per cent. The most effective salting agent at high extraction levels was $Mg(NO_3)_2$. It was found that HNO_3 , $LiNO_3$, $Cu(NO_3)_2$, $Mn(NO_3)_2$, $La(NO_3)_3$, and $Al(NO_3)_3$, which are capable of effecting appreciable salting of thorium as well as of uranium into ether, would produce markedly greater uranium extraction if thorium were absent. The divergence of the percentages of uranium extraction in the presence or absence of thorium becomes most marked at the total nitrate concentration at which the thorium begins to salt detectably into the ether. This suggests "counter salting" of the uranium from ether by other salts or acid which may also have been extracted into the ether. A similar explanation may apply to the decrease in uranium extraction encountered with thorium, aluminum, and copper nitrates at high nitrate concentrations.

In the absence of thorium the extraction effects of these salts on uranium, judged by the maximum extraction they induced within the concentration ranges studied, are as follows:

In the presence of thorium the salts, rated on the maximum uranium extraction they are capable of effecting within the limits of concentration studied, are as follows:

The relative effectiveness of these salts in producing moderate (30 to 50 per cent) extraction of uranyl nitrate into ether in the absence of thorium nitrates is as follows:

In the presence of thorium nitrate the salts, rated on their effectiveness in producing moderate (30 to 50 per cent) extraction, are as follows:

Though the percentage extraction effected by these various salts will change with different extracting solvents, it is expected that the relative salting abilities will remain the same.

Thorium extraction apparently is not detectable until the nitrate concentration is 3N to 5N, the exact normality depending on the salt. Ammonium, calcium, and magnesium nitrates effect practically no extraction of thorium within the concentration ranges studied, less than 1 per cent being extracted by the ether at the nitrate concentration giving 60 per cent extraction of uranium. Nitric acid, $\text{Al}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, and $\text{Mn}(\text{NO}_3)_2$ are marked in producing thorium extraction, as much as 54 per cent extraction occurring with $\text{Cu}(\text{NO}_3)_2$ at 11N total nitrate.

The relative effect of these salts in producing thorium extraction is as follows:

$\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ are expected to show an abrupt increase in the amount of $\text{Th}(\text{NO}_3)_4$ which is extracted from solutions of total nitrate

concentration just above those studied. $\text{Mg}(\text{NO}_3)_2$ is expected to be a stronger salting agent than $\text{Ca}(\text{NO}_3)_2$ at these higher nitrate concentrations.

A somewhat more complete study of the extraction of thorium by ether was made for solutions containing only thorium nitrate, ammonium nitrate, and nitric acid (Table 2 and Figs. 11 to 13). The extraction of thorium into ether was found to vary with nitric acid concentration, thorium concentration, and total nitrate normality. It is interesting to note that there is apparently a minimum total nitrate concentration which must be exceeded before the thorium begins to extract detectably into ether and that beyond this point the extraction occurs at an exponentially increasing rate. The effect of increasing either acid or thorium concentration above the minimum is to increase continually the percentage extraction of thorium. Nitric acid is the more marked in its effect.

In the solvent-extraction process as usually conducted, the uranyl nitrate is reextracted from the ether by washing the ether with water. Nitric acid extracted from the original salted phase by the ether would be reextracted along with the uranyl nitrate and would accumulate in the wash water, acting there as a salting agent and seriously interfering with the reextraction of uranium. To evaluate the difficulty to be anticipated an investigation was made of the nitric acid extraction into ether from solutions of ammonium nitrate, thorium nitrate, and nitric acid. The results on the extraction of nitric acid are summarized in Table 3 and Fig. 14. Up to 65 per cent of the nitric acid in the aqueous layer is extracted by ether as the total nitrate concentration reaches 12N. Varying the acid concentration between the limits 0.5N and 2N has no marked influence on the percentage of acid extracted by the ether; the absolute amount of acid extracted in this range being of course proportional to its original concentration in the aqueous phase. Thorium nitrate salts out more nitric acid into the ether than does the stoichiometrically equivalent amount of ammonium nitrate. In extractions of U^{233} by ether using ammonium nitrate as a salting agent, the total nitrate concentration is generally 8N to 10N. Under these conditions it can be assumed that the extraction of nitric acid is roughly about as complete as the uranium extraction. Data obtained by Tanret⁶ indicate that salts which were found to be strong salting agents for uranyl nitrate are also strong salting agents for nitric acid. It is therefore expected that, in general, the extent of nitric acid extraction by ether will roughly parallel the extent of uranyl nitrate extraction from an aqueous phase when there is an appreciable quantity of free nitric acid present. Hence, unless adequate

provision is made, the nitric acid thus extracted may seriously interfere in the reextraction of uranium from ether into a second aqueous phase.

3. SUMMARY

As judged by these data $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, and NH_4NO_3 would be very suitable salting agents for extraction purposes, where it is intended to free the uranium from thorium. Aluminum nitrate might be used also but would require more careful control of its concentration in order to achieve maximum uranium extraction at total nitrate normalities so low that thorium extraction has not become marked. It would be desirable to maintain low acid concentration in the aqueous phase which is to be extracted, in order to reduce both thorium and nitric acid extraction. It was found in experiments in this laboratory with a countercurrent extraction apparatus⁴ that feed solutions adjusted to pH 1.5 give optimum extraction of uranium and purification from thorium. Lower acidities result in too marked a decrease in uranyl nitrate extraction, probably resulting from hydrolysis of the uranyl nitrate into a nonextractable form.

4. ACKNOWLEDGMENT

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Table 1—Extraction of Uranium and Thorium by Ether
as Influenced by Various Salting Agents

Salting agent	Total nitrate normality	Thorium normality	Uranium extracted, %	Thorium extracted, %
HNO_3	7	1	47	
	7	1	36	21
	5	1	40	3.3
	3	1	10	0.1
	7	0	62	
	5	0	52	
	3	0	23	
LiNO_3	7.5	1	53	
	7	1	66	19
	5	1	31	
	5.5	1	25	2
	2	1	22	0
	7.5	0	81	
	5.5	0	74	
	3.5	0	36	
NH_4NO_3	2	0	10	
	12	1	59	1.2
	9	1	57	0.8
	7	1	47	0.5
	5	1	30	0.1
	3	1	8	0.0
	10	0	59	
$\text{Ca}(\text{NO}_3)_2$	5.5	0	25	
	7.50	1	96	1.2
	5.25	1	59	0.1
	4.0	1	25	0.0
	2.75	1	11	0.0
	7.50	0	99	
	4.87	0	63	
	3.62	0	32	
$\text{Mg}(\text{NO}_3)_2$	2.37	0	13	
	5.5	1	99	0.31
	4.14	1	44	0.00
	3.15	1	18.5	0.0
	2.17	1	9	0.0
	5.5	0	99	
	3.60	0	38	
	2.58	0	18	
	1.50	0	3	

Table 1—(Continued)

Salting agent	Total nitrate normality	Thorium normality	Uranium extracted, %	Thorium extracted, %
$\text{Mn}(\text{NO}_3)_2$	8.5	1	72	43
	8.5	1	70	
	7.0	1	65	
	6.0	1		5.5
	3.5	1	21.0	0.0
	7.5	0	87	
	5.0	0	74	
	2.5	0	18	
$\text{Cu}(\text{NO}_3)_2$	11.0	1	38	52
	8.0	1	62	19
	5.0	1	50	0.5
	3.0	1	12	0.0
	10.5	0	87	
	7.5	0	91	
	5.0	0	69	
	2.5	0	12	
$\text{La}(\text{NO}_3)_3$	6.5	1	39	2.1
	4.5	1	18	0.2
	4.5	1	18	
	2.5	1	5	0.0
	6.0	0	93	
	4.5	0	61	
	2.5	0	14	
$\text{Al}(\text{NO}_3)_3$	7.5	1	57	17.6
	5.5	1	63	2.8
	2.5	1	13	0.0
	6.0	0	96	
	4.0	0	54	
	2.0	0	18	
$\text{Th}(\text{NO}_3)_4$	11.0		52	11.4
	9.0		58	8.0
	5.0		32	0.14
	3.0		8	0.0

Table 2—Extraction of Thorium by Ether as Influenced by Thorium, Nitric Acid, and Total Nitrate Concentration

Initial concentrations in aqueous phase, normality			% thorium extracted by equal volume of ether
Total nitrate*	Nitric acid	Thorium nitrate	
10	1	9	30
9	0	1	0.00
9	0	2	0.11
9	0	3	0.25
9	0.5	1	0.00
9	0.5	2	0.32
9	0.5	3	0.30
9†	0.5	3	0.20
9	1.0	1	0.25
9	1.0	2	0.52
9	1.0	3	0.77
9	2.0	1	1.15
9	2.0	2	2.45
9	2.0	3	3.40
8	1.0	7	6.40
6	0.0	1	0.00
6	0.0	2	0.00
6	0.0	3	0.00
6	1.0	1	0.00
6	1.0	2	0.00
6	1.0	3	0.00
6	2.0	1	0.00
6	2.0	2	0.49
6	2.0	3	1.03
3	0	1	0.00
3	0	2	0.00
3	0	3	0.00
3	0.5	1	0.00
3	0.5	2	0.00
3	1.0	1	0.00
3	1.0	2	0.00
3	2.0	1	0.00

*The difference between the total nitrate concentration and the sum of the nitric acid and $\text{Th}(\text{NO}_3)_4$ concentrations was made up with NH_4NO_3 .

†A 50-cc batch stirred with electric stirrer 10 min. All other data on 5-cc quantities shaken by hand.

Table 3—Extraction of HNO_3 by Ether from Aqueous Solutions of Varying Acid, Ammonium Nitrate, and Thorium Concentrations

Solution composition	Total nitrate concentration of aqueous phase	% HNO_3 extracted by equal volume of ether
0.5N HNO_3 , 1.0N $\text{Th}(\text{NO}_3)_4$, varying NH_4NO_3	2.5	14
	4.5	26
	6.5	36
	8.5	50
	10.5	62
1.0N HNO_3 , 1.0N $\text{Th}(\text{NO}_3)_4$, varying NH_4NO_3	3	18
	5	31
	7	42
	9	56
	11	63
2.0N HNO_3 , 1.0N $\text{Th}(\text{NO}_3)_4$, varying NH_4NO_3	4	27
	6	36
	8	46
	10	57
	12	64
1.0N HNO_3 , 0.0N NH_4NO_3 , varying $\text{Th}(\text{NO}_3)_4$	2	11
	5	41
	8	78
	10	77

Fig. 1 — Extraction of uranyl nitrate and thorium nitrate by equal volumes of ether from solutions containing 0.5N nitric acid and varying normality of nitric acid to make up the aqueous phase to the indicated total nitrate concentration. ○, uranium extraction. ◐, uranium extraction (solution also containing 1N thorium nitrate). ●, thorium extraction (solution also containing 1N thorium nitrate).

Fig. 2 — Extraction of uranyl nitrate and thorium nitrate by equal volumes of ether from solutions containing 0.5N nitric acid and varying normality of ammonium nitrate to make up the aqueous phase to the indicated total nitrate concentration. ○, uranium extraction. ◐, uranium extraction (solution also containing 1N thorium nitrate). ●, thorium extraction (solution also containing 1N thorium nitrate).

Fig. 3—Extraction of uranyl nitrate and thorium nitrate by equal volumes of ether from solutions containing 0.5N nitric acid and varying normality of lithium nitrate to make up the aqueous phase to the indicated total nitrate concentration. ○, uranium extraction. ◐, uranium extraction (solution also containing 1N thorium nitrate). ●, thorium extraction (solution also containing 1N thorium nitrate).

Fig. 4—Extraction of uranyl nitrate and thorium nitrate by equal volumes of ether from solutions containing 0.5N nitric acid and varying normality of cupric nitrate to make up the aqueous phase to the indicated total nitrate concentration. ○, uranium extraction. ◐, uranium extraction (solution also containing 1N thorium nitrate). ●, thorium extraction (solution also containing 1N thorium nitrate).

Fig. 5—Extraction of uranyl nitrate and thorium nitrate by equal volumes of ether from solutions containing 0.5N nitric acid and varying normality of calcium nitrate to make up the aqueous phase to the indicated total nitrate concentration. ○, uranium extraction. ●, uranium extraction (solution also containing 1N thorium nitrate). ●, thorium extraction (solution also containing 1N thorium nitrate).

Fig. 6—Extraction of uranyl nitrate and thorium nitrate by equal volumes of ether from solutions containing 0.5N nitric acid and varying normality of magnesium nitrate to make up the aqueous phase to the indicated total nitrate concentration. ○, uranium extraction. ●, uranium extraction (solution also containing 1N thorium nitrate). ●, thorium extraction (solution also containing 1N thorium nitrate).

Fig. 7—Extraction of uranyl nitrate and thorium nitrate by equal volumes of ether from solutions containing 0.5N nitric acid and varying normality of manganous nitrate to make up the aqueous phase to the indicated total nitrate concentration. ○, uranium extraction. ◐, uranium extraction (solution also containing 1N thorium nitrate). ●, thorium extraction (solution also containing 1N thorium nitrate).

Fig. 8—Extraction of uranyl nitrate and thorium nitrate by equal volumes of ether from solutions containing 0.5N nitric acid and varying normality of lanthanum nitrate to make up the aqueous phase to the indicated total nitrate concentration. O, uranium extraction. ◐, uranium extraction (solution also containing 1N thorium nitrate). ●, thorium extraction (solution also containing 1N thorium nitrate).

Fig. 9—Extraction of uranyl nitrate and thorium nitrate by equal volumes of ether from solutions containing 0.5N nitric acid and varying normality of thorium nitrate to make up the aqueous phase to the indicated total nitrate concentration. ○, uranium extraction (solution also containing 1N thorium nitrate). ●, thorium extraction (solution also containing 1N thorium nitrate).

Fig. 10—Extraction of uranyl nitrate and thorium nitrate by equal volumes of ether from solutions containing 0.5N nitric acid and varying normality of aluminum nitrate to make up the aqueous phase to the indicated total nitrate concentration. ○, uranium extraction. ◐, uranium extraction (solution also containing 1N thorium nitrate). ●, thorium extraction (solution also containing 1N thorium nitrate).

Fig. 11—Influence of varying thorium nitrate concentration on the extraction of thorium nitrate by an equal volume of ether from aqueous solutions containing nitric acid, thorium nitrate, and ammonium nitrate, with the total nitrate concentration at 9N.

Fig. 12—Influence of varying nitric acid concentration on the extraction of thorium nitrate by an equal volume of ether from aqueous solutions containing nitric acid, thorium nitrate, and ammonium nitrate, with the total nitrate concentration at 9N.

Fig. 13—Influence of varying total nitrate concentrations on the thorium nitrate extraction by equal volumes of ether from aqueous solutions containing various concentrations of thorium nitrate, nitric acid, and ammonium nitrate.

Fig. 14—Extraction of nitric acid by ether as influenced by the ammonium nitrate, thorium nitrate, and nitric acid concentration of the aqueous phase. ○, extraction of nitric acid from solutions containing 0.25M thorium nitrate, 0.5N nitric acid, and varying concentrations of ammonium nitrate. △, extraction of nitric acid from solutions containing 0.25M thorium nitrate, 1.0N nitric acid, and varying concentrations of ammonium nitrate. ×, extraction of nitric acid from solutions containing 0.25M thorium nitrate, 2.0N nitric acid, and varying concentrations of ammonium nitrate. ●, extraction of nitric acid from solutions containing 1N nitric acid and varying concentrations of thorium nitrate.

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Paper 3.12

A SURVEY OF SOLVENTS FOR EXTRACTION OF U^{233} AND Pa^{233} FROM NEUTRON-IRRADIATED THORIUM

By Earl K. Hyde and Michael J. Wolf

[Editor's Note: Contribution from the Argonne National Laboratory. Based on Report CB-3810. Prepared for publication Apr. 30, 1947. The uranium extraction was done by E. K. Hyde, and the protactinium extraction was done by M. J. Wolf.]

ABSTRACT

A survey of organic solvents has been made to determine their ability to extract trace concentrations of uranium and protactinium from aqueous nitrate systems, with their possible use in a solvent-extraction process for U^{233} production in mind.

The extraction effected by a number of the best solvents, particularly ketones, has been studied under a variety of conditions. The results are presented in curves, tables, and text discussions.

1. INTRODUCTION

The preparation of U^{233} involves the irradiation of thorium with neutrons. The absorption reaction and the subsequent decay are as follows:

The separation of the trace concentrations of U^{233} thus produced from the large bulk of the thorium may be effected by one of the following schemes:

Scheme 1. Separation of U^{233} directly when the Pa^{233} has completely or nearly completely decayed.

Scheme 2. Separation of both Pa^{233} and U^{233} away from thorium before complete decay of Pa^{233} , followed by (a) a separation of U^{233} and Pa^{233} and (b) the complete decay of Pa^{233} into U^{233} .

Scheme 3. Separation of Pa^{233} alone at an early date after short irradiation so that no significant amount of U^{233} has formed, following which the Pa^{233} is permitted to decay.

Scheme 3 has little to recommend it for large-scale preparations but is useful for the preparation of small samples of very pure U^{233} . A number of processes for the chemical separation of protactinium from thorium have been considered. Schulze¹ has studied a fluoride volatilization method; Katzin and Stoughton² have studied a manganese dioxide precipitation method; and Steahly and Stoughton³ have studied an iodate precipitation method. Several others have made similar studies.

Solvent extraction applied according to scheme 1 or scheme 2 is the type of process which has received most consideration for large-scale production of U^{233} . Some of the reasons for this are the following: A solvent-extraction process is comparatively simple, an important feature when operations must be carried out by remote control because of the biological hazard from the highly radioactive solutions. A solvent-extraction process can be made quite specific. Previous studies on the solvent extraction of heavy elements from nitrate solutions have shown that excellent separation from the lighter element impurities and from radioactive fission products can be achieved. Chemical procedures might well require many steps to effect the same degree of separation. A solvent-extraction process could probably be operated with considerably higher recovery of the products. With a suitably designed countercurrent extraction column, nearly complete recovery of the final products could be expected, while losses in a process based on precipitations would be difficult to keep below several per cent.

The solvent extraction of uranium, particularly by ethyl ether, has been studied extensively by others. Much of the information available is not directly applicable to the extraction of trace concentrations of uranium from gross amounts of thorium because most of the studies do not consider the behavior of thorium and most of them deal with the extraction of gross amounts of uranium.

Fontana was the first to study the use of ether extraction in U^{233} isolation.⁴ Hellman and Wolf⁵ made a thorough laboratory study of the ether extraction of trace concentrations of uranium with the requirements of this problem in mind. Based on their studies extensive laboratory operations have been carried out by Hagemann, Studier, and Katzin,⁶ by Hagemann,⁷ and by others. These studies completely dem-

onstrate the feasibility of large-scale production of U^{233} by scheme 1 using an ethyl ether extraction process.

The only serious objection to the ethyl ether process is the obvious one of the inflammability of the solvent, but experience in commercial production of uranium has shown that this is not an insuperable obstacle. It was desirable, however, to find alternate solvents.

This report gives the results of a study of the ability of organic solvents, other than ethyl ether, to extract trace concentrations of uranium and protactinium from nitrate solutions, with a view toward their possible use in the separation of U^{233} by one of the schemes discussed above. Very little or no information on the solvent extraction of protactinium had been reported up to the time of this study; the discovery of good solvents for protactinium nitrate may find many applications other than the specific one under consideration.

A solvent suitable for U^{233} isolation must have acceptable physical characteristics; a low distribution coefficient (solvent to aqueous) for thorium nitrate, radioactive daughters of thorium, fission products, and inert impurities; and a high distribution coefficient for uranyl nitrate. If scheme 1 is to be used, a low extraction coefficient for protactinium salts is necessary, whereas for scheme 2 a high extraction coefficient for protactinium salts is necessary. In addition to these requirements the commercial availability of the solvent must be considered.

In preliminary studies those solvents which have undesirable physical characteristics, such as high water solubility, high viscosity, long settling times, and dangerous inflammability, and those which exhibit chemical instability toward aqueous nitrate solutions were eliminated from consideration. Solvents surviving these preliminary tests were examined for their ability to extract trace concentrations of uranyl and protactinium nitrates and gross amounts of thorium nitrate. Those solvents found to extract more than a few per cent of thorium nitrate were eliminated from further study regardless of their ability to extract uranium and protactinium. A few of the most promising were tested under a variety of conditions.

2. EXPERIMENTAL PROCEDURE

Concentrated stock solutions of thorium nitrate, nitric acid, ammonium nitrate, and several other nitrate salts were prepared. The proper amounts of these solutions and of distilled water were delivered from burets to a 15-ml, calibrated, glass-stoppered centrifuge cone to make 5 ml of solution of a desired composition. To this solution U^{233} tracer (5,000 to 10,000 c/min at 52 per cent counting

yield) or Pa^{233} tracer (10,000 to 300,000 c/min at 10 per cent counting yield) was added.

After shaking the solutions for 5 min with 5 ml of solvent, the layers were cleanly separated by centrifugation, and aliquots of the solvent were pipetted into separate centrifuge cones for analysis.

To a 2-ml aliquot was added excess saturated oxalic acid in 1N HCl to precipitate thorium oxalate. The oxalate, and hence the thorium, was determined by dissolving the washed precipitate with slight heating in an excess of standard ceric sulfate and back-titrating with standard ferrous ammonium sulfate to the ferroin end point.

The method of separating and determining the tracer contained in an aliquot of the solvent varied. In most of the uranium experiments the technique was to reextract 0.5 ml of the solvent with 0.5 ml of distilled water in a 5-ml centrifuge cone, freeze the aqueous layer in a dry ice-acetone bath, and discard the stripped solvent layer. Then the water layer was evaporated on a platinum disk, and the alpha-disintegration rate was measured in a standard-pulse ionization chamber. This method was very successful when the solvent extracted very little thorium (2 per cent or less). When thorium extraction was moderately high, it was necessary to separate thorium. To the water extract of the solvent aliquot obtained by evaporation of the solvent over water (if it was volatile enough), by steam distillation, or by use of the above freezing technique, a few drops of 6N HF were added to precipitate ThF_4 . The supernatant solution was evaporated on platinum disks and counted. A 10 per cent correction was applied for uranium lost on the thorium fluoride.

In the protactinium experiments separation of the thorium was unnecessary. The protactinium in 0.25- to 2.0-ml aliquots of solvent was returned to an aqueous solution by volatilization or steam distillation of the solvent. In the case of a few high-boiling solvents such as *o*-nitroanisole and nitrobenzene, these methods were too slow, and the solvent was extracted twice with water. In all cases the aqueous phase left after removal of the solvent was evaporated directly on a platinum plate or on a 1-in.-diameter watch glass. The dry samples were counted on the standard Geiger-Mueller beta counter. Evaporation of aliquots of solvent directly on watch glasses by the aid of a heat lamp was unsatisfactory.

In every experiment in which thorium nitrate was a constituent of the aqueous layer, a "blank" run on a solution identical except for the absence of tracer was necessary to determine the extent of extraction of thorium-decay-product activities. This correction could be quite high for a solvent which extracted much thorium nitrate.

In the protactinium experiments nitric acid extraction was estimated on a separate aliquot of the solvent layer by direct titration with standard alkali, using phenolphthalein or methyl orange indicator. In the presence of appreciable quantities of thorium the acid was determined by potentiometric titration using a Beckman pH meter and glass electrode. The first inflection point in the titration curve, which occurs between pH 2 and pH 3, indicating the point where thorium begins to interfere, is taken as the end point of the acid base titration. This end point necessitates a correction of about 3 per cent to the experimental values. More frequently the nitric acid extraction was determined by adding an excess of standard sodium hydroxide to the aliquot of solvent and back-titrating with standard acid to the phenolphthalein end point. The amount of base used up by the thorium could be corrected for, since, from potentiometric titration of known thorium nitrate solution, it had been determined that one equivalent of thorium reacts with 0.89 equivalent of hydroxyl ion.

In some of the protactinium experiments it was possible to check the reliability of the results by studying the material balance of the beta-active tracer. Reasonably good material balances were secured by evaporating and counting 20- μ l samples of the aqueous salt layers. In dry residues from concentrated salt solutions, however, the error due to self-absorption was appreciable.

3. EXPERIMENTAL RESULTS

The results of a preliminary survey of a wide range of solvents with the composition of the aqueous phase arbitrarily standardized at 2N thorium nitrate, 1N nitric acid, and 3N ammonium nitrate are listed in Table 1. The more promising solvents were subjected to more detailed study; the results are presented in curves and tables. Note that all extraction figures refer to equal volumes of solvent and aqueous phase.

4. DISCUSSION

4.1 General Comparison of Solvent Classes. The data of Table 1 reveal that ethers (other than ethyl ether), halogen compounds, and nitro compounds are not useful for the extraction of either uranium or protactinium.

The Cellosolve derivatives in general are good extracting solvents for uranium, but they are unsatisfactory because they extract too much thorium. In addition, undesirable physical characteristics, such as long settling times and a tendency to form emulsions, argue against

their use. The best Cellosolve derivative is dibutyl carbitol, but the data of Table 2 show that even it extracts too much thorium.

The alcohols are only mediocre extracting solvents for uranium, and such extraction as they do show drops off rapidly with the length of the carbon chain. A number of the longer-chain alcohols, however, are excellent solvents for protactinium. Special mention may be given *n*-heptanol, 2-ethyl hexanol, and *n*-octanol. Because of its very low thorium extraction, 2-ethyl hexanol was selected for more complete study; the results are presented in Fig. 21. These long-chain alcohols are open to some objection because of their physical characteristics.

The esters as a class are fairly promising, but, since the extraction of uranium seems to drop off markedly with increasing molecular weight, only the acetates and propionates need be given serious consideration. A trend toward higher protactinium extraction with increasing length of the alcohol half of the ester is apparent. However, the percentage of protactinium extraction does not reach a high figure. It would be difficult to effect a clean-cut separation according to either scheme 1 or 2 using an ester.

Esters suffer from the further objection of being susceptible to acid hydrolysis. The curves of Fig. 3 show that this hydrolysis tends to increase both uranium and thorium extraction. The ester is about 25 per cent hydrolyzed under the conditions of the higher extraction. Several experiments carried out to determine whether the addition of ethyl alcohol or acetic acid to ethyl acetate or other solvents would raise the uranium extraction gave inconclusive results.

As a class the ketones excelled all the other solvents investigated. The lower-molecular-weight ketones, as well as the alicyclic ketones, extract too much thorium; but the three ketones methyl *n*-amyl ketone, methyl isobutyl ketone, and diisopropyl ketone are excellent. Of these diisopropyl ketone is the best.

4.2 Analysis of the Extraction by Ketones. The extraction effected by the three ketones mentioned above was studied under a variety of conditions. The important features of the data presented in the curves and tables will be pointed out in the following analysis.

(a) Influence of Nitric Acid on Extraction. Nitric acid has markedly different effects on the extraction of uranium, thorium, and protactinium. As long as the total nitrate concentration is maintained constant, the extraction of trace uranium is insensitive to changes in acid concentration for concentrations above 0.1N. Thorium extraction, on the other hand, is quite sensitive to acid concentration, and the percentage extraction can be increased severalfold by raising the acid concentration from 0.1N to 1N. Table 3 and Figs. 8 and 9 illustrate clearly these differing behaviors. The extraction of trace

protactinium is the most sensitive of all to acid concentration. When the acidity is low, very little extraction occurs even in the presence of a high concentration of a powerful, neutral salting agent. When the acidity is raised to 1N, the use of the same salting agent results in 80 per cent extraction (see Fig. 19). Even without the assistance of neutral salting agents, high extraction can be attained in nitric acid solutions (see Fig. 14).

In the studies made at low acid concentrations it was noted that appreciable amounts of free nitric acid were liberated, presumably by hydrolysis of thorium nitrate. Where nitric acid was introduced with the tracer to the extent of 0.06N (curve 2, Fig. 19), electrometric pH determinations on relatively concentrated salt solutions showed that the hydrogen-ion activity was in all cases greater than 0.06N and rose markedly with increase in salt concentration. At high salt concentrations such measurements may be considerably in error, but the general trend of the observations is confirmed by ketone extraction data on the same solutions (Fig. 12). At the higher salt concentrations more acid was extracted into the solvent layer than had been added to the aqueous layer.

To counteract this rise in acid concentration due to hydrolysis, a series of solutions was prepared in which the acid concentration was carefully adjusted to pH 1.4 to 1.6 with ammonium hydroxide (curve 3, Fig. 19). Less than 1 per cent of the protactinium tracer was extracted from these solutions.

Advantage could be taken of the differing effect of nitric acid concentration on uranium and protactinium extraction to separate uranium from protactinium and thorium by operating at a pH of 1.5 and then, by raising the acidity to 1N, to separate protactinium from thorium with the same solvent.

(b) Effect of Neutral Salting Agents on Extraction. Nitrate salts added to the aqueous layer have quite different effects on the shape of the extraction curves for protactinium, thorium, and uranium.

Increasing amounts of various nitrate salts, keeping the acid concentration constant at 1.0N, results in an abrupt rise in the protactinium-extraction curves. The curves level off to a maximum of 70 to 80 per cent at a total nitrate concentration of 2N to 3N for divalent and trivalent cations and at a total nitrate concentration of about 5N for a monovalent cation. High protactinium extraction can be obtained without a high aqueous salt concentration.

This is in contrast to the uranium-extraction curves, which rise more gradually and show a greater dependence on the nature of the neutral salting agent. The leveling off at a maximum extraction is not reached until the total nitrate concentration is greater than 5N.

This maximum is higher and is reached earlier when di- and trivalent cations are used than when ammonium ion is used.

The thorium-extraction curves rise only gradually as the total nitrate concentration is increased until a certain concentration is exceeded, after which the extraction goes up rapidly. When the higher-valent salting agents are used, this rapid rise comes at a lower total nitrate normality, and the extraction of thorium reaches a higher value.

(c) Extraction of Nitric Acid. Considerable nitric acid is extracted by the ketone from the aqueous layer with which it is in contact. The nature and concentration of the neutral salt and the concentration of the acid in the water layer influence the amount of acid which will be extracted (see Fig. 18). The extraction of nitric acid probably has an important role in the extraction of heavy element nitrates.

(d) Reextraction from the Solvent. The reextraction of uranium and thorium from a ketone solution is readily effected by contact of the ketone with pure water or with dilute acid. Protactinium can be re-extracted in the same way, but because of a steep rise in the curve of protactinium extraction vs. acidity (see Fig. 14) not much acid may be used in the aqueous wash solution. The effect of acid reextracted from the ketone must also be considered. The effect of reducing the acid concentration of the water layer on the reextraction of protactinium from diisopropyl ketone is shown in Table 4. With a 10/1 ratio of ketone to water, the distribution coefficient is only one-half as great as with a ratio of 1/1, where the acid is more highly diluted. When the nitric acid concentration is still further reduced by a preliminary water extraction of the solvent layer, the distribution coefficient rises to 86.

However, the use of pure water for the reextraction of protactinium has one disadvantage. It has been found that protactinium so removed cannot be extracted again upon acidifying and salting the aqueous solution and contacting it with an organic solvent because of a conversion of the protactinium to an unextractable state. Prolonged treatment with hot concentrated acid is necessary to reconvert the protactinium to an extractable condition.

5. SUMMARY

Preliminary examination of the ability of a large number of organic solvents to extract trace amounts of uranyl nitrate and protactinium nitrate from nitrate solutions revealed a number of promising solvents, principally aliphatic ketones. The influence of the concentration of nitric acid and the nature and concentration of nitrate salts

in the aqueous phase on the extraction effected by these solvents was studied in detail. In addition, the extent of extraction of gross amounts of thorium nitrate and nitric acid was studied.

Consideration was given to the application of these solvents to the large-scale production of U^{233} from neutron-irradiated thorium. The choice of a solvent and of extracting conditions requires a careful consideration of the factors studied above; the experimental results indicate that some sacrifice in extraction must be made if clean separation from thorium and other impurities is to be effected.

6. ACKNOWLEDGMENT

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Table 1 — Preliminary Survey: Uranyl Nitrate and Thorium Nitrate Extraction under "Standard" Conditions*

Solvent	% U extraction	% Th extraction	% Pa extraction
Ethers			
Ethyl ether	35	0.0	0.19†
<i>n</i> -Propyl ether	2.2	0.0	0.10
Dibutyl ether	1.6	0.0	0.05
Cellosolve derivatives			
Diethyl cellosolve	55	24	
Dibutyl carbitol	59	2.7	0.15†
Benzyl cellosolve		21	
2-Ethyl butyl cellosolve	59	7	
Alcohols			
<i>n</i> -Butanol	44	5.2	
<i>sec</i> -Butyl carbinol	30	0.6	
Diethyl carbinol	24	0.7	
Heptanol	24	0.65	71.5†
Methyl <i>n</i> -amyl carbinol	36–50	4.7	
Disopropyl carbinol	11.6	0.0	
<i>n</i> -Octanol		0.5	74.8
2-Ethyl hexanol		0.0	72.1
Heptadecanol		0.0	31.7
Ketones			
Methyl ethyl ketone	47	22	
+ 15% xylene			
Methyl <i>n</i> -propyl ketone	53	11	
Methyl isobutyl ketone	57	20	20.9†
Disopropyl ketone	56	0.3	48.7†
Methyl <i>n</i> -amyl ketone	47	0.9	3.0†
Cyclohexanone		11	
Methyl cyclohexanone		Large	

Table 1—(Continued)

Solvent	% U extraction	% Th extraction	% Pa extraction
Esters			
Ethyl acetate	43	0.6	0.26†
<i>n</i> -Propyl acetate	50	1.3	9.1
Isopropyl acetate	54	1.2	11.9
<i>sec</i> -Butyl acetate	39		22.2
<i>n</i> -Butyl acetate	39	0.06	10.6
Isobutyl acetate	21	0.02	0.18
<i>n</i> -Amyl acetate	31	0.3	31.9†
Methyl propionate	10–20	0.2	0.06
Ethyl propionate	22	0.03	0
Ethyl butyrate	10	0	
2-Ethyl butyl acetate	9	0.02	
Diethyl malonate	22		
Methyl benzoate	7.5	0	
Halogen and nitro compounds			
Trichloroethane	0	0	0
Trichloroethylene	1.5	0.2	
Chloroform	0	0	
2-Nitropropane	3.5	Trace	0.25
Nitrobenzene	2.1	Trace	0.10
<i>o</i> -Nitroanisole	3.5	Trace	0
Miscellaneous			
Dimethyl dioxane	34	3.8	
Isophorone		27	
Mesityl oxide		12.7	

*1N HNO₃, 3N NH₄NO₃, 2N Th(NO₃)₄.†1N HNO₃, 2N NH₄NO₃, 2N Th(NO₃)₄.‡1N HNO₃, 2N Al(NO₃)₃, 3N Th(NO₃)₄.

Table 2—Extraction Data for Dibutyl Carbitol

Initial aqueous composition				Extraction	
Th(NO ₃) ₄ norm	HNO ₃ norm	NH ₄ NO ₃ norm	Total NO ₃ ⁻ norm	% Th extracted	% U extracted
3	0.5	0	3.5	0.08	28
3	0.5	3.5	7.0	2	52
3	0.5	6.5	10.0	14.5	
3	0.0	4.0	7.0	0.6	47.5
3	0.5	3.5	7.0	2.0	52.5
3	1.0	3.0	7.0	2.7	59.4
3	2.0	2.0	7.0	9.1	58.2
1	0.5	5.5	7.0	0.75	43.8
2	0.5	4.5	7.0	0.83	52.0
3	0.5	3.5	7.0	2.0	52.5

Table 3—Effect of Acid Concentration on Extraction by Methyl *n*-Amyl Ketone

Th(NO ₃) ₄ norm	HNO ₃ norm	NH ₄ NO ₃ norm	Total NO ₃ ⁻ norm	% Th extraction	% U extraction
2	0*	4	6	0.05	37
2	1	3	6	0.9	47
2	2	2	6	1.4	44
2	4	0	6	3.6	45

*Beckman pH reading 1.0 to 1.5.

Table 4—Reextraction of Protactinium from Diisopropyl Ketone into Water

Composition of aqueous layer	Ratio of volumes, <u>water</u> <u>ketone</u>	Initial conditions ketone layer		Pa distribution coefficient, <u>water</u> <u>ketone</u>
		Th(NO ₃) ₄ millieq./ml	HNO ₃ millieq./ml	
2N sodium sulfate	0.1	0.153	1.18	15
2N sodium sulfate	1	0.153	1.18	30

Fig. 1—Extraction of U²³³ tracer, ○, and thorium, □, by isopropyl acetate from aqueous solutions 2N in Th(NO₃)₄, 1N in HNO₃, and varying normality in NH₄NO₃.

Fig. 2—Extraction of U^{233} tracer, $\circ$, and thorium, $\square$, by *n*-propyl acetate from aqueous solutions 2N in $Th(NO_3)_4$, 1N in HNO_3 , and varying normality in NH_4NO_3 .

Fig. 3—Extraction of U^{233} tracer, $\circ$, and thorium, $\square$, by ethyl acetate from aqueous solutions 1N in $Th(NO_3)_4$, 1N in HNO_3 , and varying normality in NH_4NO_3 . $\circ$ and $\square$, separation of phases immediately after equilibration, $\circ$ and $\square$, 20-hr contact of phases before analysis.

Fig. 4—Extraction of thorium by methyl *n*-amyl ketone. Composition of aqueous phase: ○, 1N in $\text{Th}(\text{NO}_3)_4$, varying normality in $\text{Mg}(\text{NO}_3)_2$; □, 2N in $\text{Th}(\text{NO}_3)_4$, 1N in HNO_3 , varying normality in NH_4NO_3 .

Fig. 5—Extraction of U^{233} tracer by methyl *n*-amyl ketone. Composition of aqueous phase: ○, 1N in $\text{Th}(\text{NO}_3)_4$, varying normality in $\text{Mg}(\text{NO}_3)_2$, pH 1.0 to 1.5; □, 2N in $\text{Th}(\text{NO}_3)_4$, 1N in HNO_3 , varying normality in NH_4NO_3 .

Fig. 6—Extraction of U^{233} tracer by methyl isobutyl ketone. Composition of aqueous phase: ○, 1N in $Th(NO_3)_4$, varying normality in $Ca(NO_3)_2$, pH 1.0 to 1.5; □, 1N in $Th(NO_3)_4$, 1N in HNO_3 , varying normality in NH_4NO_3 .

Fig. 7—Extraction of thorium by methyl isobutyl ketone. Composition of aqueous phase: ○, 1N in $Th(NO_3)_4$, varying normality in $Ca(NO_3)_2$; □, 1N in $Th(NO_3)_4$, 1N in HNO_3 , varying normality in NH_4NO_3 .

Fig. 8—Extraction of U^{233} tracer by diisopropyl ketone. Composition of aqueous phase: ○, 1N in $Th(NO_3)_4$, 1N in HNO_3 , varying normality in $Ca(NO_3)_2$; △, 1N in $Th(NO_3)_4$, varying normality in $Mg(NO_3)_2$, pH 1.0 to 1.5; ◻, 1N in $Th(NO_3)_4$, 1N in HNO_3 , varying normality in NH_4NO_3 (◻-S, low count due to self-absorption); ×, 1N in $Th(NO_3)_4$, varying normality in $Al(NO_3)_3$, pH 1.0 to 1.5.

Fig. 9—Extraction of thorium by diisopropyl ketone. Composition of aqueous phase: ○, 1N in $Th(NO_3)_4$, 1N in HNO_3 , varying normality in $Ca(NO_3)_2$; ●, 1N in $Th(NO_3)_4$, 1N in HNO_3 , varying normality in $Mg(NO_3)_2$; △, 1N in $Th(NO_3)_4$, varying normality in $Mg(NO_3)_2$, pH 1.0 to 1.5.

Fig. 10—Extraction of thorium by diisopropyl ketone. Composition of aqueous phase: □, 1N in $\text{Th}(\text{NO}_3)_4$, 1N in HNO_3 , varying normality in NH_4NO_3 ; ×, 1N in $\text{Th}(\text{NO}_3)_4$, varying normality in $\text{Al}(\text{NO}_3)_3$, pH 1.0 to 1.5.

Fig. 11 — Extraction of Pa^{233} tracer (curve 1) and of thorium (curve 2) from solutions 3N in $\text{Th}(\text{NO}_3)_4$, 2N in $\text{Al}(\text{NO}_3)_3$, and varying normality in HNO_3 .

Fig. 12 — Extraction of HNO_3 by diisopropyl ketone indicating hydrolysis of $\text{Th}(\text{NO}_3)_4$. Composition of aqueous phase: 3N in $\text{Th}(\text{NO}_3)_4$, varying normality in $\text{Mg}(\text{NO}_3)_2$, 0.06N in HNO_3 added.

Fig. 13 — Extraction of Pa^{233} tracer by diisopropyl ketone. Composition of aqueous phase: curve 1, 1N in HNO_3 , varying normality in NH_4NO_3 ; curve 2, 1N in HNO_3 , varying normality in $\text{Mn}(\text{NO}_3)_2$; curve 3, 1N in HNO_3 , varying normality in $\text{Al}(\text{NO}_3)_3$.

Fig. 14—Extraction of Pa^{233} tracer by diisopropyl ketone from dilute HNO_3 .

Fig. 15 — Extraction of Pa^{233} tracer (curves 1 and 2), thorium (curve 5), and nitric acid (curves 3 and 4) by diisopropyl ketone. Composition of aqueous phase: curves 1, 4, and 5, 1N in HNO_3 , 3N in $\text{Th}(\text{NO}_3)_4$, varying normality in $\text{Ca}(\text{NO}_3)_2$; curves 2 and 3, 1N in HNO_3 , varying normality in $\text{Ca}(\text{NO}_3)_2$.

Fig. 16—Extraction of Pa^{233} tracer (curves 1 and 2) and thorium (curve 3) by diisopropyl ketone pretreated by contact with a tracerless aqueous solution of the same composition. Composition of aqueous phase: curves 1 and 3, 1N in HNO_3 , 1N in $\text{Th}(\text{NO}_3)_4$, varying normality in $\text{Mg}(\text{NO}_3)_2$; curve 2, 1N in HNO_3 , varying normality in $\text{Mg}(\text{NO}_3)_2$.

Fig. 17—Extraction of Pa^{233} tracer (curves 1 and 2), thorium (curves 5 and 6), and nitric acid (curves 3 and 4) by diisopropyl ketone. Composition of aqueous phase: curves 1, 4, and 5, 1N in HNO_3 , 2N in $\text{Th}(\text{NO}_3)_4$, varying normality in NH_4NO_3 ; curves 2, 3, and 6, 0.5N in HNO_3 , 2N in $\text{Th}(\text{NO}_3)_4$, varying normality in NH_4NO_3 .

Fig. 18—Extraction of nitric acid by diisopropyl ketone. Composition of aqueous phase: curve 1, varying normality in HNO_3 ; curve 2, 1N in HNO_3 , varying normality in NH_4NO_3 , curve 3, 1N in HNO_3 , varying normality in $\text{Ca}(\text{NO}_3)_2$; curve 4, 0.5N in HNO_3 , 2N in $\text{Th}(\text{NO}_3)_4$, varying normality in NH_4NO_3 .

Fig. 19—Extraction of Pa^{233} tracer by diisopropyl ketone. Composition of aqueous phase: curve 1, 1N in HNO_3 , 2.5N in $\text{Th}(\text{NO}_3)_4$, varying normality in $\text{Mg}(\text{NO}_3)_2$; curve 2, 0.06N in HNO_3 added, 3N in $\text{Th}(\text{NO}_3)_4$, varying normality in $\text{Mg}(\text{NO}_3)_2$; curve 3, 3N in $\text{Th}(\text{NO}_3)_4$, varying normality in $\text{Mg}(\text{NO}_3)_2$, pH 1.5.

Fig. 20—Extraction of thorium by diisopropyl ketone. Composition of aqueous phase: curve 1, 1N in HNO₃, 2.5N in Th(NO₃)₄, varying normality in Mg(NO₃)₂; curve 2, 0.06N in HNO₃ added, 3N in Th(NO₃)₄, varying normality in Mg(NO₃)₂; curve 3, 3N in Th(NO₃)₄, varying normality in Mg(NO₃)₂, pH 1.5.

Fig. 21 — Extraction of Pa^{233} tracer (curve 1), thorium (curve 3), and HNO_3 (curve 2) by 2-ethyl hexanol from aqueous solutions 1N in HNO_3 , 3N in $\text{Th}(\text{NO}_3)_4$, and varying normality in $\text{Ca}(\text{NO}_3)_2$.

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Paper 3.13

SOLVENT EXTRACTION OF U^{233} FROM HIGHLY
RADIOACTIVE MATERIAL; A REMOTELY CONTROLLED
LABORATORY-SCALE APPARATUS

By French Hagemann

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ABSTRACT

Remotely controlled apparatus for separation of U^{233} from neutron-irradiated thorium "oxycarbonate" on the scale of $\frac{1}{2}$ kg of carbonate per day has been developed. Using countercurrent solvent extraction, with diethyl ether as the solvent, a thorium-uranium separation factor of 10^6 and decontamination factors for beta and gamma activity from 10^5 to 10^6 have been obtained with 99.5 per cent recovery of uranium.

1. INTRODUCTION

Irradiation of thorium with slow neutrons produces U^{233} according to the following reactions:

Seaborg, Gofman, and Stoughton¹ first isolated microgram amounts of U^{233} from thorium which had been bombarded with neutrons from the Berkeley cyclotron by separating Pa^{233} and allowing it to decay to U^{233} . The first milligram quantities of U^{233} which were made available by the use of the pile as a high-intensity neutron source were separated directly by a batch ether extraction process.² As greater

quantities of material became available, the need for a more efficient and less tedious method of separation became apparent. To this end laboratory-size equipment was developed for dissolution, filtration, neutralization, and countercurrent solvent extraction. This equipment could be operated behind substantial lead shielding and permitted continuous separation of U^{233} , present in concentrations of less than 50 ppm, from irradiated thorium oxycarbonate on the scale of $\frac{1}{2}$ kg of carbonate per day. The apparatus to be described has been used successfully over a period of many months and has proved convenient, safe, and efficient.

The separation process for which the apparatus was designed is outlined in Fig. 1.

Since each can of thorium oxycarbonate, after irradiation in a graphite-moderated pile for several months at a power level of about 4000 kw, has associated with it some 50 curies of beta and 25 curies of gamma activity, due chiefly to 27.4-day Pa^{233} (reference 3), adequate shielding of the extraction apparatus is imperative if the material is to be handled within a few months after removal from the pile. It has been found² experimentally that the half thickness of the activity is approximately $\frac{1}{8}$ in. of lead; 2 in. of lead have provided sufficient protection in this apparatus. This shielding necessitates remote-control operation of the process up through the extraction of uranium into diethyl ether, at which point the activity has been reduced to a safe level.

Solvent extraction by means of a packed column employing the countercurrent principle has been adopted as more suitable than a batch process because of the advantages with regard to efficiency of separation and adaptability to continuous remote-control operation.

The aluminum, thorium, and ammonium nitrates formed in the solution and neutralization steps furnish sufficient salting-out effect upon uranium⁴ so that additional salting agents are unnecessary. The distribution coefficient for uranium between the ether and aqueous phases, $C(\text{ether})/C(\text{aqueous})$, lies between 1 and 2 for the feed solutions used; that for thorium lies between 10^{-3} and 10^{-4} . The pH of the feed solution is rather critical for good thorium-uranium separation. The amount of thorium extracted increases rapidly with decreasing pH, while the amount of uranium extracted decreases markedly when the pH exceeds about 1.7. The optimum value lies in the range pH 1.4 to 1.6. Extraction of $Al(NO_3)_3$, NH_4NO_3 , and protactinium are negligible under these conditions, and decontamination factors (ratio of initial to final Geiger-Mueller counts per minute per unit weight of uranium) for combined beta and gamma activities of 10^5 to 10^6 are obtained.

The amount of thorium which is extracted by the ether is reduced considerably by utilizing a short "scrub" section at the top of the extraction column. Using 4 ft of packed extraction section and 28 in. of scrub section, with 9N NH_4NO_3 as the scrub solution and a solvent to feed to scrub ratio of 6:2:1, less than 0.0001 per cent of the thorium in the feed is extracted by the ether, corresponding to about 99 per cent purity for the separated uranium. If the scrub section is not used, about 0.1 per cent of the thorium is extracted at a solvent to feed ratio of 2/1. Extraction of uranium is greater than 99 per cent in both cases at feed throughputs up to 600 ml/hr.

The uranium is recovered from the ether by reextracting counter-currently into pure water. Since the rate of flow of water necessary for essentially complete recovery of uranium is $\frac{1}{20}$ of the feed flow rate, a volume reduction of twentyfold is effected in the extraction process. The aqueous uranium solution is evaporated, and final purification is carried out on a 1- to 10-ml scale.

The extremely high distribution coefficients for uranium between sulfate solutions and ether permit reextraction of a large amount of ether by a small static volume of $(\text{NH}_4)_2\text{SO}_4$ solution. Using 3N $(\text{NH}_4)_2\text{SO}_4$ as the "stripping" solution, volume reductions of several hundredfold may be obtained. In this case separation of uranium from the sulfate solution by precipitation with ammonium hydroxide is necessary before final purification can be carried out.

2. DESCRIPTION OF APPARATUS

A diagrammatic sketch of the apparatus is shown in Fig. 2. Appropriately placed mirrors, not shown in the drawing, permitted observation of the parts of the equipment surrounded by lead shielding. The lead partitions between the components of the apparatus allowed necessary repairs or adjustments in one section while active material was present in the others. Stopcocks and joints in that part of the system handling aqueous solutions were lubricated with Apiezon N; those in the solvent line with a starch-glycerol paste.

2.1 Dissolver. A 6-liter flat-bottomed flask with a 55/50 standard taper joint sealed on the neck served as the dissolver. Heat was supplied to the flask by a small hot plate controlled by a Variac outside the lead cave. A small water-cooled condenser fitted with a standard taper joint was attached to the flask to prevent evaporation losses during the dissolution process.

2.2 Filtration Assembly. The large end of the filter tube, which was 15 to 20 cm long and 15 mm in diameter, was packed with alternate layers of glass wool and diatomaceous filter aid. The upper end

of the tube was connected by a short length of Tygon tubing to a semi-ball joint which connected with the line leading to the 3-liter round-bottomed suction flask. The ball joint was held in place by a spring clamp fashioned from a large battery clip. New filter tubes were prepared outside the cave and then placed in position with the aid of long-handled tongs.

2.3 Neutralization Flask. Adjustment of the pH of the feed solution was made in a 5-liter flask fitted with an electrically driven stainless steel stirrer. Reagents were introduced through an addition tube not shown in the drawing. Samples of the solution were removed through the sampling port for pH measurements; by use of a single-drop glass electrode these measurements could be carried out on samples small enough to make shielding unnecessary.

2.4 Extraction Column. The countercurrent extraction column was 22 mm I.D. and was packed with $\frac{1}{8}$ in. I.D. glass helices supported on nichrome or stainless steel wire spirals. The packed extraction section was 4 ft in length, and the packed scrub section was 28 in. Semiball joints permitted easy disassembly for cleaning and repacking. The solvent-aqueous interface was controlled manually by adjustment of the position of the raffinate overflow.

2.5 Recovery Columns. The countercurrent recovery column was 18 mm I.D. and was packed to a height of 3 ft with $\frac{1}{8}$ in. helices. The interface was controlled manually.

A semicontinuous batch column of 16 mm I.D. was used with $(\text{NH}_4)_2\text{SO}_4$ as a stripping solution. It was packed with 26 in. of $\frac{1}{8}$ -in. helices and was provided with a stopcock at the bottom to permit drainage.

2.6 Pumping System. Feed and scrub solutions and solvent were pumped to the extraction column by means of a bellows-type metering pump, which is described elsewhere.⁵ Corrosion of the brass pump parts by the aqueous solutions was prevented by filling the bellows units with carbon tetrachloride. In the case of the radioactive feed solution the necessity for shielding the pump was eliminated by maintaining the carbon tetrachloride-aqueous interface within the lead cave. Solvent and aqueous solutions were delivered to the column under pressure, thus eliminating the extra height which would be necessary for gravity feed. Air-ballast reservoirs constructed from 300-ml round-bottomed flasks served to smooth out the pulsating discharge from the pumps.

Rotameters (Fisher and Porter tubes No. 000 for the aqueous solutions and No. 0000 for the ether) fitted with stainless steel floats were used to measure rates of flow. The meter tubes were connected into the line with semiball glass joints to facilitate removal for cleaning.

The rate of introduction of water into the countercurrent recovery column was controlled by displacement of water from a cylinder by means of a plunger which was lowered at a constant rate of about 0.025 in./min by a suitably geared electric motor. The rate of flow could be varied by using plungers of various diameters; a plunger 25 mm O.D. gave a flow of 20 ml/hr.

2.7 Solvent Recovery Apparatus. A 2-liter round-bottomed flask fitted with an efficient water-cooled condenser was used for distillation of the washed ether prior to recycling. The flask was heated by a Glas-Col heating mantle controlled with Variac.

3. PROCEDURE

3.1 Loading. The aluminum cans containing the active thorium oxycarbonate were loaded directly into the dissolving flask with long-handled tongs; a bed of powdered solid CO_2 in the bottom of the flask served to cushion the fall and to prevent breakage. The transfer was done behind temporary lead shielding in the case of extremely active material. Up to five cans, each containing about 200 g of carbonate, could be handled at one time.

3.2 Dissolution. After the CO_2 had evaporated (the evaporation was speeded by use of a heat lamp and a stream of air), the condenser was attached to the flask, and the aluminum jackets and contents were dissolved in nitric acid. Once started, the reaction of the nitric acid and aluminum is extremely vigorous and difficult to control. The best procedure has been found to be to first add about 250 ml of water, containing a small amount of mercuric nitrate to act as a catalyst, followed by 25 to 50 ml of concentrated HNO_3 . The mixture was allowed to stand for a short time, with heating if necessary, until the reaction started. After the initial reaction subsided, concentrated HNO_3 was added in small portions until further addition produced no violent reaction. Sufficient acid could then be safely added to give an excess over the amount calculated to dissolve the thorium oxycarbonate and aluminum of 30 to 50 ml of 16N HNO_3 per 100 g of carbonate. The mixture was boiled until the thorium had gone into solution, leaving only a slight flocculent residue of silicious impurity (chiefly from the aluminum can); several hours of boiling were usually required. The solution was then diluted with water to a volume of about 300 ml per 100 g of ThOCO_3 and allowed to cool.

3.3 Filtration. The solution was filtered by application of suction from a water aspirator to the suction flask, thus drawing the liquid through the filter tube. A properly packed tube would filter cleanly at the rate of about 1 liter per hour. When packed too tight the filter

tended to clog rapidly, and if it was packed too loose the filtration was incomplete. Used tubes were stored inside the lead shielding since a large amount of the beta and gamma activity, particularly that due to Pa^{233} , remained adsorbed on the insoluble material.

3.4 Adjustment of pH. After proper adjustment of stopcocks by means of a special long-handled tool the filtered solution was transferred to the neutralization flask by application of pressure to the suction flask. Ammonium hydroxide and water were added in an amount such that the pH as measured by the glass electrode was 1.4 to 1.6, and the final solution volume was approximately 1000 ml per 200 g of ThOCO_3 . The resulting solution was about 2.5N to 3.0N $\text{Th}(\text{NO}_3)_4$, 2.0N to 2.5N $\text{Al}(\text{NO}_3)_3$, 1N to 2N NH_4NO_3 , and 10^{-5}N $\text{UO}_2(\text{NO}_3)_2$. The 9N NH_4NO_3 used as the scrub solution was also adjusted to pH 1.4 to 1.6 by addition of nitric acid.

3.5 Solvent Extraction. The solvent-aqueous interface was maintained at the top of the extraction column. When ether was made the continuous phase, the extraction efficiency was low owing to preferential wetting of the packing by the aqueous phase, resulting in a decrease of contact area between the two phases.

Flow rates were set at 2 to 2.5 parts of solvent to 1 part of feed when the scrub section was not used and at 6 parts solvent to 1 part of scrub to 2 parts of feed when the scrub was used. Under these conditions throughputs of 600 ml/hr in the first case and 400 ml/hr in the latter were well below the flood points. Once the rates were set and the interface adjusted, little or no further attention was required.

The interface in the countercurrent recovery column was also maintained above the packed section. At a flow rate of 20 ml/hr for the water and 1200 ml/hr for the ether effluent from the extraction column, the recovery of uranium was 99.5 per cent.

When the semicontinuous recovery column was used it was filled with 70 ml of 3N $(\text{NH}_4)_2\text{SO}_4$ solution. This amount of solution would extract all the uranium (and thorium) from the ether up to the point where thorium ammonium sulfate started to precipitate in the column. For 0.1 per cent thorium extraction or less, as was the case when the scrub section was not utilized, the uranium from 15 to 25 liters of feed solution could be completely extracted in one 70-ml filling.

3.6 Solvent Recovery. The washed ether was distilled before recycling. A layer of water was kept in the distilling flask to prevent the small amount of nitric acid carried over by the ether from becoming so concentrated as to react with the ether. Any uranium which was not removed in the recovery column was recovered from

this water layer. The entire extraction process could be operated on 2 liters of ether, with sufficient make-up to take care of evaporation losses.

3.7 Final Separation and Purification. The water solution of uranium from the countercurrent recovery column was evaporated to dryness, and the final purification was effected by small-scale batch ether extractions and suitable precipitation procedures designed to give the degree of purity desired.

When $(\text{NH}_4)_2\text{SO}_4$ solution was used for reextraction, an excess of NH_4OH was added. The precipitated $(\text{NH}_4)_2\text{U}_2\text{O}_7$ and $\text{Th}(\text{OH})_4$ were centrifuged and washed, dissolved in nitric acid, and reprecipitated to ensure removal of any sulfate carried down in the first precipitation. After dissolution in nitric acid final purification was carried out as above.

4. DISCUSSION OF RESULTS

The data given in the tables indicate the results which have been obtained with the apparatus in actual use. The figures given in Table 1 are for a run on material which had been removed from the pile seven months prior to extraction. Rates of flow were 500 ml/hr for the feed and 1200 ml/hr for the solvent. The scrub section was not used, and reextraction was in 3N $(\text{NH}_4)_2\text{SO}_4$ solution.

Table 2 gives results on material which had a four-month "cooling" time. The scrub section was used, and the flow rates were 400 ml/hr of feed, 200 ml/hr of scrub, and 1200 ml/hr of solvent. Uranium was recovered by countercurrent reextraction into water at a flow rate of 20 ml of water per hour.

Direct assay of the feed solution or the raffinate for U^{233} by alpha counting was impossible because of the high salt concentration and the presence of considerable amounts of alpha-emitting thorium daughters. The procedure used for the raffinate was to extract a 1- to 5-ml sample with three double portions of ether, wash the ether with 7N $\text{Ca}(\text{NO}_3)_2$ or 10N NH_4NO_3 solution, evaporate over water, plate, and count for alphas. A blank obtained by a similar extraction of a solution having the same composition but with no uranium present was subtracted, and a correction was applied for yield which was determined by extracting a similar solution "spiked" with a known amount of U^{233} .

The values of alpha counts per minute for the feed solutions given in the tables were calculated from the total amount of U^{233} recovered plus the loss in the waste streams.

The thorium separation factor was calculated by dividing the thorium/uranium ratio of the feed solution by the ratio of thorium to uranium in the product obtained from the recovery column.

Table 1

	Acid concentration	Thorium concentration	Alpha c/min/ml	Geiger-Mueller c/min/ml
Feed	pH = 1.6	~2.8N	63,000	2.72×10^7
Raffinate		~2.8N	111	
Ether effluent from extraction column	0.0035N	0.0009N	25,800	100
Ether effluent from recovery column		None detectable	2	23
Uranium loss in extraction column			0.18%	
Uranium loss in recovery column			<0.01%	
Thorium separation factor			1.2×10^3	
Decontamination factor			6.2×10^5	

Table 2

	Acid concentration	Thorium concentration	Alpha c/min/ml	Geiger-Mueller c/min/ml
Feed	pH = 1.4	~2.6	96,000	1.76×10^9
Raffinate	pH = 1.9	~2.6	292	
Ether effluent from extraction column	0.0041N		31,700	4,100
Ether effluent from recovery column	0.00026N		158	2,400
Product effluent from recovery column		1%* of U^{233}	1.9×10^6	48,000
Uranium loss in extraction column			0.46%	
Uranium loss in recovery column			0.50%	
Thorium separation factor			1.7×10^6	
Decontamination factor			8.1×10^5	

* Spectrographic analysis by F. Tompkins.

Fig. 1 — U^{233} -separation process. The thorium oxycarbonate used was a mixture of oxycarbonate and partly hydrated oxides containing about 82 per cent of thorium.

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Fig. 2—Remote-control extraction apparatus.

The decontamination factor was calculated by dividing the Geiger-Mueller counting rate per milliliter of the feed solution by the amount of such activity held up in the recovery column per milliliter of feed. A correction was made for the Geiger-Mueller activity associated with the U^{233} itself.⁶ For the geometry and absorber used, this correction amounted to 25 Geiger-Mueller counts per 10,000 U^{233} alphas.

The results obtained for material which was extracted only one week after removal from the pile were similar to those illustrated in the tables, except that a much smaller percentage of the beta and gamma activity which was extracted by the ether was reextracted in the recovery column. Although this difference has not been investigated experimentally, it is probable that it may be accounted for by the presence of relatively ether-soluble short-lived fission products, such as iodine, which would have decayed away in the material which had been out of the pile for several months.

The high pH value of the raffinate from the extraction column indicates considerable extraction of nitric acid from the feed solution during passage through the column. Since the distribution coefficient for uranium C(aqueous)/C(ether) starts to decrease appreciably around pH 1.8, it appears likely that some improvement in extraction efficiency would be obtained by preacidification of the solvent in order to maintain the acidity of the aqueous phase throughout the column.

The 0.5 per cent loss in the countercurrent recovery column could be reduced by increasing the water flow rate or by lengthening the column; however, since the uranium carried in the washed ether can be recovered, this loss is only apparent.

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Paper 3.14

A LABORATORY METERING PUMP

By French Hagemann and Nison N. Hellman

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ABSTRACT

A laboratory metering pump of the bellows type is described with variable rates of flow of 0 to 8 liters per hour.

The efficient operation of a countercurrent solvent-extraction column demands a means of continuously delivering solvent and solutions to the system at rates of flow that can be accurately varied and controlled. On a laboratory scale the rates of flow required may range from a few cubic centimeters to several liters per hour.

A mechanical metering pump has many obvious advantages over devices which depend upon stopcocks or constant head for control of flow. In the absence of a suitable commercially available model meeting these requirements, a pump has been designed and constructed which has proved very satisfactory in actual use.

The details of construction are shown in Fig. 1. The three bellows units, which are readily replaceable in case of failure, are mounted so that all are driven by the same electric motor. The brass bellows are soft-soldered to the standard brass flare fittings. Connection to the glass system is made with the aid of a neoprene gasket.

Independent variation of the discharge rate of each unit is accomplished by raising or lowering the plug upon which the bellows rests, thus varying the displacement of each stroke. An inner spring assembly returns the bellows to its original position at the completion

of the cycle. Adjustments may be made during operation to any rate of flow from 0 to about 8 liters per hour, and once set the rate remains essentially constant.

Corrosion of the metal parts is prevented, when acid aqueous solutions are being handled, by filling the bellows unit with carbon tetrachloride. Noncorrosive solvents or solutions are put into the pumping unit.

Pumping is effected by transmission of the motion of the liquid in the bellows to the set of glass check valves. The pulsating discharge may be smoothed out in the case of gravity feed by pumping into an open line which contains a suitable constriction. When the pumping is done against a slight pressure, an air-ballast tank serves to give an even flow.

This pump has been in actual use for more than 500 hr, handling acid salt solutions and diethyl ether at rates from 200 to 2000 ml/hr without requiring attention and with no failure of the bellows.

Fig. 1—Bellows-type laboratory metering pump.

Paper 3.15

ISOLATION OF THE FIRST MILLIGRAM QUANTITIES OF U^{233}

By French Hagemann, Martin H. Studier, and Leonard I. Katzin

[Editor's Note: This paper was a contribution of the Argonne National Laboratory and is based on Report CB-3703.]

ABSTRACT

A description is given of the preparation of the first milligram quantities of U^{233} by means of a batch-by-batch ether extraction of the nitrate. The remotely operated apparatus is illustrated.

A half life of 1.61×10^5 years is reported for U^{233} from direct weighing-counting measurements.

1. INTRODUCTION

It was reported in 1934 that neutron bombardment of thorium gave, among others, a beta activity of about 15 min half life.¹ Later it was confirmed that this activity was associated with the thorium fraction itself,²⁻⁴ and the half life was more accurately determined as 24 min.² A beta activity of about 25 days half life which was found to grow in this material was announced⁵ in 1938 to be Pa^{233} . Doubt about the identity of these activities, which arose from the discovery of fission by Hahn and Strassmann,⁶ was removed by the work of Von Grosse, Booth, and Dunning⁷ and Seaborg, Gofman, and Kennedy.⁸ Seaborg, Gofman, and Stoughton⁹ followed the complete chain,

and showed that U^{233} was an alpha emitter with a half life of about 1.2×10^5 years.

Uranium²³³ was isolated by the last-mentioned workers in microgram amounts from thorium nitrate which had been irradiated with the neutrons formed when beryllium was bombarded with deuterons in the Berkeley 60-in. cyclotron. Production of much larger amounts of U²³³ has been made possible by the use of high neutron fluxes in the chain-reacting uranium pile. This paper describes the method used for the isolation of the first milligram quantities of U²³³ which were produced by irradiation of thorium in the graphite-moderated pile at the Clinton Laboratories.¹⁰

2. EXPERIMENTAL WORK

The thorium was irradiated in the form of a mixture of basic carbonate and partly hydrated oxide. Thorium "carbonate" furnished by the Lindsay Light & Chemical Co. was found by analysis to contain relative amounts of carbon dioxide, water, and thorium dioxide which were consistent with a composition of 50 per cent ThOCO₃·H₂O and 50 per cent of an equimolar mixture of hydroxide and oxide. Ammonium carbonate was also present. By heating this material for 24 hr at 200°C the carbonate content was reduced to about 20 per cent, most of the remaining 80 per cent consisting of oxide. The product contained 82 to 83 per cent thorium by weight and was found to possess the necessary properties of stability to heat generated in the pile and solubility in nitric acid.

The heat-treated carbonate was formed into pellets 1.1 in. in diameter and about 1 in. high by means of a special die to which pressures of 25 to 40 tons/sq in. could be applied. A solution of stearic acid in acetone was used as a lubricant for the die. The resulting pellets weighed about 50 g each and had a density of 3 to 3.5 g/cc. The pellets were packed, four to a can, into aluminum cans, which were then welded shut and placed in the pile.

There are 20 curies of beta activity associated with each milligram of Pa²³³ and approximately half as much gamma activity.¹¹ Since the material from which the U²³³ was to be extracted had been irradiated for about seven months at a neutron flux of the order of 2×10^{11} /sec-cm² and had been removed from the pile less than two half lives of Pa²³³ before the extraction, several tenths of a milligram of Pa²³³ were expected to be present in each can. This made some shielded, remotely controlled extraction procedure necessary.

Seaborg, Gofman, and Stoughton⁹ did not isolate U²³³ directly. They wished to obtain a product free from other isotopes of uranium. Since the quantity of thorium which was bombarded contained milligram amounts of natural uranium impurity, they separated the few micro-

grams of Pa^{233} which were produced upon MnO_2 carrier, purified it from uranium, and allowed it to decay to U^{233} .

However, direct separation of the uranium was feasible for the pile-irradiated material under discussion since the quantity of U^{233} formed was much larger than the relatively small amount of U^{238} impurity in the thorium (less than 1 ppm). Ether extraction of the uranium (as uranyl nitrate) from the protactinium and the bulk of thorium was chosen as the most adaptable procedure after consideration of experiments by Fontana.¹² Dissolution of the thorium carbonate together with the aluminum jacket in nitric acid furnished a solution containing thorium, aluminum, and ammonium nitrates which had sufficient "salting-out" effect upon uranium, such that about 65 per cent of the latter was extracted by an equal volume of ether. The extracted uranium was accompanied by less than 1 per cent of the thorium and negligible amounts of protactinium and fission products. The apparatus used for dissolving the material and performing the extraction is shown in Fig. 1 and is described below.

Absorption in lead of the gamma radiations from the irradiated carbonate was determined roughly by measuring the intensity of the radiation penetrating various thicknesses of lead placed over two cans of the material. As seen in Table 1, the half thickness for this mixed hard radiation is about $\frac{1}{8}$ in. of lead. In accordance, the extraction apparatus was surrounded by a shield constructed from dovetailed lead brick 2 in. thick to provide adequate protection from radiation.

Later a lead absorption curve on a sample of pure Pa^{233} , determined by using a Geiger-Mueller tube wrapped in lead to eliminate scattered radiation, indicated the presence of a gamma ray of 328 Kev energy. There was no evidence of a 1.5-Mev gamma ray as reported by Stoughton;¹¹ this was probably a scattering artifact. An 80-Kev gamma ray and L x-rays were also detected.

3. DESCRIPTION OF APPARATUS

The solution flask A was a 6-liter flat-bottomed flask fitted with a removable condenser and delivery-tube assembly. The extraction flask B was constructed from a 500-ml Kjeldahl flask. Measured volumes of aqueous solution could be introduced into the extraction flask by means of the calibrated buret so that the liquid surface level was just below the tip D. A 20-liter bottle H, placed inside a stone crock as a safety precaution, served as a storage vessel for extracted solution. The apparatus was observed indirectly through suitably placed mirrors for remote-control operation.

4. PROCEDURE

The general procedure was the following: The solution flask, with condenser head removed, was filled about one-third full with powdered CO_2 ice. By means of long tongs one or two cans of irradiated material were dropped into the flask upon the cushion of ice. Following evaporation of the dry ice, the condenser head was set in place, and concentrated nitric acid diluted with an equal volume of water was added through the condenser. The acid contained about 0.1 g of mercuric nitrate to act as a catalyst for the dissolution of the aluminum jacket. After the aluminum was partly dissolved, sufficient nitric acid to give an acid concentration of 2N to 3N after complete solution of the thorium was added, and the mixture was refluxed until only a flocculent precipitate of SiO_2 (impurity in the aluminum) remained undissolved. The solution was then made up to the desired final volume and total nitrate concentration and allowed to cool.

The solution of the first can to be extracted was made up to a volume of 2 liters with ammonium nitrate solution so that the final concentration was about 1N in nitric acid, 1.4N in thorium nitrate, 1.1N in aluminum nitrate, and 5.5N in ammonium nitrate.

Other experiments at this time¹³ indicated that the same uranium extraction could be attained without the addition of ammonium nitrate if the aluminum and thorium nitrate concentrations were increased and that reduction of the acid concentration markedly reduced the amount of thorium extracted. For the subsequent extractions the final volume of solution was reduced to 1 liter per can, and the excess nitric acid over 0.1N to 0.2N was neutralized with ammonia.

By application of air pressure through the top of the condenser, 160-ml portions of solution were transferred to the extraction flask. Each portion was extracted three times with 250-ml portions of ether. The two phases were stirred for 3 to 5 min and allowed to stand for a few minutes to allow separation; then the ether layer was removed into a Kjeldahl flask by applying suction at F (Fig. 1). Each ether portion was extracted with a 100-ml portion of water, then reextracted with 50 ml of water, and reused to extract the active solution. A fresh 50-ml water wash was used for each batch of active solution, but the same 100-ml wash was used for several batches. Separation of the ether from the water washes was accomplished by immersing the flask in a dry ice-acetone mixture, freezing the aqueous phase, and pouring off the ether.

The water washes containing the U^{233} were concentrated by evaporation; after sufficient ammonium nitrate had been added to make the

solution 10N, the washes were reextracted with ether. Repetition of the extraction two or three times was sufficient to purify the uranium completely from thorium and protactinium.

Ten cans of the irradiated thorium were worked up in this manner and yielded 48 mg of U^{233} (as determined by radioactive assay using 21,100 dis/min/ μ g as the specific activity of pure U^{233}) as the uranyl nitrate free from chemical impurities.

Samples of the material were reduced electrolytically in HCl solution with platinum electrodes, the anode being separated by an asbestos fiber to prevent reoxidation by the liberated chlorine, and the uranium was precipitated as UF_4 by addition of HF solution. The precipitate was centrifuged, washed with water and alcohol, and finally ether- and air-dried. Mass-spectrographic analysis of these samples by Dempster and coworkers¹⁴ showed the material to be 96.4 per cent U^{233} and 3.6 per cent U^{238} . The presence of the latter isotope is due to natural uranium impurity in the thorium oxycarbonate starting material.

Determination of the specific activity of this material by Hyde¹⁵ gave a value of 20,360 dis/min/ μ g, which, after applying a correction for the isotopic purity of the material, gives 1.61×10^5 years for the half life of U^{233} . The value 1.2×10^5 years determined by Seaborg, Gofman, and Stoughton⁹ by measuring the alpha-activity growth from a measured amount of Pa^{233} of known half life is reasonably close to this more accurate figure.

Table 1—Absorption of Radiation Following Primary Filtration through 3 to 4 Cm of H_2O and $\frac{3}{8}$ In. of Lead

Lead thickness, in.	Radiation intensity, arbitrary units
$\frac{3}{8}$	195
$\frac{1}{2}$	95
$\frac{5}{8}$	46
$\frac{3}{4}$	19
$\frac{7}{8}$	16

Fig. 1—Apparatus for extraction of U^{233} . (A) Solution flask. (B) Extraction flask. (C) Buret. (D) Tip. (E, F) Points at which suction is applied. (H) Aqueous-waste storage vessel.

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Paper 3.19

A CONTINUOUS-BATCH SOLVENT-EXTRACTION APPARATUS

By French Hagemann

[Editor's Note: This paper was a contribution of the Argonne National Laboratory and is based on Report CN-3640.]

ABSTRACT

Apparatus is described for extraction by immiscible solvents which permits continuous replacement of both solvent and solution to be extracted.

Devices for extraction by immiscible solvents have been described by Wollner and Matchett.¹ These consist of a mixing chamber, in which the solution to be extracted is dispersed in the solvent, and a connected separation chamber from which the extracted solution is bled at the same rate as the feed solution is introduced into the mixing chamber. However, since the volume of solvent in such a device is small and fixed in amount, the recovery of solute is incomplete except when the distribution coefficient of the solute is greatly in favor of the solvent phase.

A modified apparatus (Fig. 1) has been designed. It utilizes two separation chambers and allows continuous replacement of the solvent, as well as of the solution to be extracted, thus permitting more complete extraction of the solute. Solvent and feed are introduced continuously directly into the mixing chamber A. A high-speed stainless steel centrifugal-type stirrer efficiently disperses the two phases, drawing the liquid from the bottom of the chamber and forcing it through the small side tubes. The less dense phase separates in chamber B and overflows at the same rate as it is fed into the mixer. Disengagement of the heavier phase takes place in chamber C. The sliding joint D was constructed from a 2-ml pyrex hypodermic syringe

by sealing tubing onto the inner and outer barrels and blowing a hole in the bottom of the inner barrel. The joint permits adjustment of the level of the overflow from chamber C, which controls the volume of liquid in the mixing chamber.

The apparatus has been used to extract small amounts of uranium with diethyl ether from aqueous solutions containing thorium, aluminum, and ammonium nitrates and has performed satisfactorily. At flow rates up to 500 ml of feed solution and 1000 ml of ether per hour the equilibration of feed and solvent has been efficient, as indicated by recovery of the amount of uranium calculated from experimentally determined distribution coefficients, and the separation of the two phases has been clean and sharp.

Fig. 1—Continuous-batch solvent-extraction apparatus. (A) Mixing chamber. (B) Collecting chamber. (C) Collecting chamber. (D) Sliding joint.

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Paper 3.20

STUDY OF THORIA SLURRIES

By Nison N. Hellman

[Editor's Note: This paper was a contribution of the Metallurgical Laboratory at the University of Chicago and is based on part of Report CC-3056.]

The neutron irradiation of heavy water-thorium oxide slurries for the purpose of producing U^{233} offers nuclear and engineering advantages in pile design. The feasibility of piles using such a slurry system rests upon the possibility of producing a slurry of thorium oxide which possesses stability toward radiation and would possess the proper physical and chemical characteristics necessary for trouble-free operation. Preliminary investigations were therefore made of the chemical and physical nature of water-dispersed thorium oxide systems.

The physical requirements for a satisfactory thoria slurry are as follows:

1. Density of thoria in the slurry such that it would contain 1 g of Th per milliliter (equivalent to 1.13 g of ThO_2 per milliliter).
2. Low settling velocity, in order to prevent the development of a cake in stagnant portions of the apparatus or, in the case of a temporary shutdown, to prevent the blockage of the circulating system.
3. Fluidity sufficiently great to permit easy, efficient, and rapid pumping.
4. Time stability or the ability of the slurry to maintain its good character for protracted periods of time (several months) under intensive radiation.
5. Nonerosive nature, so that the circulating system would not be worn away, weakening the apparatus and introducing impurities into the system.

The chemical characteristics of a satisfactory slurry are as follows:

1. Stability to heat and radiation.
2. Stability toward peroxide formed from the water as a result of radiation.
3. High chemical purity with respect to neutron-absorbing elements.
4. Noncorrosive nature.

Thorium oxide may be obtained from the ignition of its oxyacid salts or from the hydroxide. Material prepared at low temperatures may be amorphous; crystalline material may be obtained from higher temperature ignitions. Thus precipitated hydroxide dried at temperatures up to 340°C is amorphous, but oxide obtained by ignition of the hydroxide at 1050°C , or the nitrate or oxalate at 750°C , is crystalline with the same radiograms in all cases.¹ Thoria is hygroscopic and absorbs gases, although calcination at very high temperatures somewhat reduces this tendency. Thorium oxide crystals belong to the cubic system. The specific gravity of thoria has been variously reported from 9.2 to 10.2, the deviations being attributable to entrained air or moisture and to the presence of impurities in the oxide.

Assuming that the specific gravity of thorium oxide is about 10.2, a slurry which contained 1 g of thorium per milliliter would contain about 11 per cent by volume ThO_2 . According to data obtained by workers under C. F. Hiskey in a section studying UO_3 hydrate slurries, the smallest particle size² from which slurries (11 per cent by volume) suitable for pumping in circulating lines can be formed is approximately $1\ \mu$. Slurries of this concentration formed of finer particles would, according to these data, be too viscous. Because of the importance of variables affecting the properties of the surface in controlling the properties of systems composed of particles of this size range and smaller, this $1\text{-}\mu$ limit is only a rough indication of the magnitude of a lower limit to the particle size which would be suitable.

The settling rates of particles of various size are of interest because of the primary importance of having a stable slurry. The settling velocities given in Table 1 were calculated for 25°C by means of a Stokes' law sedimentation formula, assuming the density of the hydrated ThO_2 particles to be 9. Again it would appear that a desirable slurry from the standpoint of settling rate should consist of particles about $1\ \mu$ in radius.

A further consideration necessitating fine particle size lay in the need for a nonerosive slurry. Hiskey and coworkers² showed that suspensions of quartz containing particles above $5\ \mu$ for aluminum

and above $30\ \mu$ for 18-8 stainless steel cause excessive erosion. It was concluded therefore, on the basis of the requirements for a thorium slurry, that experimental studies would be confined to systems composed of thorium particles less than $10\ \mu$ in radius.

Experimental investigations of thorium slurries were to be made using two different types of thorium. One type was a special grade of calcined thorium of high purity purchased from the Lindsay Light & Chemical Co.; the other was a fused thorium containing considerable carbide impurity, obtained from the Norton Company. The calcined thorium from Lindsay was a fine powder, more than 50 per cent by weight passing a 325-mesh sieve. This material was ground further by ball milling with steel balls overnight; after this treatment the material was composed entirely of particles less than $10\ \mu$ in size.

The fused thorium was coarse, average grain size being about 1 to 2 mm. This material was first crushed in a mullite mortar to pass a 100-mesh sieve. Then one portion was ground by means of mortar and pestle to pass a 325-mesh sieve (less than $50\ \mu$). Another portion was ball milled overnight using steel balls. After this treatment the material completely passed through a 325-mesh sieve. The fused thorium was then boiled in 6N nitric acid for 2 hr in order to destroy thorium carbide. The thorium was washed free of nitric acid by four washings with a double volume of water and six washings with a double volume of 95 per cent ethyl alcohol.

It was intended for these preliminary studies to consider three-size fractionated systems composed of particles 1 to 10, 0.1 to 1, and less than $0.1\ \mu$ in radius. Fractionation of the 1- to $10\text{-}\mu$ material was accomplished by sedimentation. The fine dry thorium preparations were suspended in water and stirred for 1 hr by a high-speed stirrer in order to break up any temporary aggregates. The material was then given a brief but thorough stirring and allowed to settle for a period long enough (as calculated by Stokes' law) for all particles greater than $10\ \mu$ in radius to settle the distance from the top of the suspension to the bottom of the container. The supernatant suspension was then decanted, and the residue was made up again with water. This process of stirring briefly, settling, and decanting was repeated 10 to 20 times in order to completely free the suspension from particles greater than $10\ \mu$ radius. The collected supernatants were combined and in turn stirred briefly and allowed to settle, this time for a period long enough for all particles of greater than $1\ \mu$ radius to settle through the length of the suspension. After repeated dispersions (20 to 30 times) a residue was obtained which was composed of particles 1 to $10\ \mu$ in size.

It was observed that, although suspensions of the mortar-ground fused thorium and of the ball-mill-ground calcined thorium behaved

similarly, dispersing well in water and flocculating in 95 per cent ethyl alcohol, the ball-mill-ground fused thoria flocculated in water and would disperse in alcohol. The reason for this unusual behavior is not clear.

The collected supernatants from the 1- to 10- μ fractionation are the starting material for securing the 0.1- to 1.0- μ material. Sedimentation is accomplished by centrifugation in an International No. 2 centrifuge equipped with a head carrying 250-ml bottles. Calculations of settling rates were made using an integrated form of Stokes' law.

The supernatants from the centrifugation contained a small yield of material less than 0.1 μ in radius. This was flocculated by acidifying the solution with nitric acid ($\sim 1N$) and allowing it to settle. The flocculent sediment was then redispersed in water and washed with alcohol by a centrifugation-decantation technique in order to free it of nitric acid.

The water-wet fractions were next washed with absolute methyl alcohol and then with toluene and finally dried from toluene at 70°C. This treatment was intended to provide a dry, fluffy powder of the same size distribution as that present in the dispersed state. Electron-microscope pictures of this material showed that the fractionations were generally successful. In the case of the less than 0.1- μ material it appears that pronounced aggregation occurred.

The experimental observations on the three-size fractionated systems will be discussed separately. Physical observations include measurement of density, settling volume, and viscosity. Chemical studies were barely begun at the time work had to be concluded and consist of fragmentary studies of the effect of peroxide on thoria slurries. Data were secured only on the Lindsay calcined thoria systems, the size separation of the fused thoria just being concluded at the time work was stopped.

Systems Composed of Thoria, 1 to 10 μ in Radius. Slurries of material this size are characterized by a rapid settling rate and low surface activity. The data for Lindsay calcined thoria are given here. The density of the thoria is about 9.1 ± 0.2 . The kinematic viscosity of the slurries up to a concentration of 1.5 g of ThO_2 per milliliter, the limit studied, is about equal to that of water; thus a slurry containing 1 g of ThO_2 per milliliter has a relative viscosity about twice that of water. Settling is so rapid that turbulent currents are produced in the suspension which limit the rate of settling. In concentrated suspensions the thoria settles as a mass, the upper boundary moving with a rate of about 10 cm/min. The settling volume is about 1.2 ml/g. The sediment is a hard, difficultly dispersable cake. From a physical standpoint this is not a very desirable slurry material because of its rapid settling rate and cake-forming property.

Tests in which peroxide was used on these slurries produced little effect. Treatment with even 30 per cent H_2O_2 did not cause any noticeable change in settling rate, settling volume, or viscosity. Decomposition of the peroxide by thoria is vigorous if the system is allowed to become warm. One anomalous peroxide treatment will be described in detail because of its unusual results. In this test a 150 per cent excess of peroxide with respect to conversion of all the thoria into thorium peroxide was added to a slurry with rapid stirring. The final concentration was about 1 g of thoria per milliliter of suspension, and the suspension was stirred overnight. The resulting product was an extremely granular material (average grain size about 0.5 mm) formed by aggregation of the finer material. On drying, these granules broke up easily although they were stable against vigorous stirring when wet. No tests at higher than room temperatures were conducted of peroxide-thoria systems.

Systems Composed of Thoria, 1 to 0.1 μ in Radius. Slurries of material this size are characterized by moderately slow settling rate and the initial appearance of some surface active properties. For the Lindsay calcined thoria the density was again 9.1 ± 0.2 , no decrease in density being observed for this finer material. The kinematic viscosity of the suspensions up to 1.2 g of ThO_2 per milliliter, the limit studied, was again equal to that of water; relative viscosity in a system containing 1 g of ThO_2 per milliliter was about twice that of water.

This material was slow settling in concentrated suspensions; thus in a slurry containing 1.0 g of ThO_2 per milliliter the upper boundary of the massively settling material moved at a rate of about 1 cm/hr. The settling volume is about 2.6 ml/g, more than twice as great as that for the 1- to 10- μ material. The sediment is fluffy and readily dispensable. The sedimentation is analogous to the shrinkage occurring in the syneresis of a gel, in that fractures occur in the sediment; yet no thixotropy could be revealed by measurement of viscosity at various shearing rates. Systems of this type would be, from a physical standpoint, very suitable for slurries, being of low enough viscosity to pump, yet relatively nonsettling and readily dispersable. A sample in suspension for four months showed no apparent change in properties.

The stability of this material toward peroxide also appears good. It promotes the decomposition of peroxide at a faster rate than the coarser material. Treatment even with 30 per cent peroxide, which was kept cool to prevent excessive frothing, appears to decompose the peroxide slowly without the thoria undergoing any change. If the reaction was allowed to proceed at a rapid rate, frothing occurred. No

detailed high-temperature studies of this stability toward peroxide were made when this work was closed.

Systems Composed of Thoria, Less Than $0.1\ \mu$ in Radius. Experimental studies of this fraction were limited by the extremely small amount of material available. Slurries containing 1.59 g of ThO_2 per milliliter are stiff; however, slurries containing 1.0 g of ThO_2 per milliliter are quite free flowing. An insufficient amount of material was available to permit viscosity measurements. This material is nonsettling and coats the wall of tubes or glassware very tightly. It apparently does not react with peroxide, though it will decompose peroxide, frothing if reaction is vigorous. Judging from electron-microscope pictures, it is probable that the material for these tests may well be about $0.5\text{-}\mu$ aggregates of very fine material instead of a disperse system of less than $0.1\text{-}\mu$ thoria; hence generalizations on these data are restricted.

It appears from these preliminary results that slurry systems might offer considerable promise of sufficient physical and chemical stability to be suitable for pile purposes. No judgment on their suitability toward radiation can be made until tests are made of these slurries under intensive radiative bombardment.

Table 1—Settling Velocity of Various Sizes of Thoria Particles
in Water at 25°C Calculated by Means of Stokes' Law

Particle radius, μ	Time required to sediment 10 cm
0.1	1438 hr
1.0	86.3 min
10.0	51.0 sec
20.0	12.75 sec
50.0	2.04 sec

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Paper 6.1

ANALYSIS OF ORE RESIDUES FOR IONIUM AND PROTACTINIUM

By Leonard I. Katzin, Q. Van Winkle, and Jacob Sedlet

[Editor's Note: This paper was a contribution from the Argonne National Laboratory and is based on Report CC-3744.]

1. INTRODUCTION

With the availability of large amounts of pitchblende-ore residues, resulting from the processing of uranium for atomic power developments, it has been possible to consider the recovery of long-lived members of the uranium and actinium radioactive decay series in appreciable amount. In addition to being of intrinsic interest these materials are of use as radiation sources and as sources of other isotopes. This report deals with analysis of some residue fractions which have not previously been considered as sources for protactinium (Pa^{231}) and ionium (Th^{230}) but which may prove to be convenient sources of these materials.

The isotope Pa^{231} occurs in nature approximately to the extent that radium (Ra^{226}) occurs, which is about 0.15 ppm in pitchblende ore containing about 60 per cent by weight of U_3O_8 . The sum total of this material which has been extracted and purified, according to literature reports, is probably not significantly more than 2 g, considerably less than the amount of radium recovered.

After initial manipulations pitchblende ores are usually treated with sulfuric acid and sodium nitrate, giving an acidic solution of uranyl salts (and other salts) with an insoluble residue in which is found the radium. Some polonium, ionium, and protactinium dissolve with the uranium. A fraction at least of the protactinium presumably remains with the insoluble gangue since protactinium has been obtained from such material. Von Grosse¹ and Graue and Kaeding² used the ultimate

residues following removal of the radium as their sources of protactinium.

The acid solution of uranyl nitrate is treated with excess sodium carbonate to precipitate some of the nonuranium materials appearing in solution, the uranium remaining in solution as the carbonate complex. It is to be expected that the protactinium dissolved in the first step should precipitate with the other hydroxides and carbonates at this point. The behavior of ionium is less definite, since thorium forms a soluble carbonate complex under the proper conditions. It seems likely that there might be at least a partial precipitation at this point. The analytical data bear out this presumption.

The carbonate solution of uranium is then treated with NaOH to precipitate uranium, and the uranium is dissolved in acid and reprecipitated with ammonia. It is to be expected that any protactinium and ionium present in the carbonate solution would follow the uranium through these steps. The ammonium diuranate is next calcined to U_3O_8 , the oxide is dissolved in nitric acid, and the concentrated nitrate solution is extracted with ether. The ether solution of uranyl nitrate is washed repeatedly with portions of water until no further UX_1 activity (Th^{234}) can be detected. After steps are taken for recovery of additional uranium from the washes and original solution, the residual solutes are combined and saved together with any insoluble residue from the treatment of the oxide with nitric acid. It is therefore to be expected that this residue may be a rich source of ionium if an appreciable portion survives the carbonate precipitation.

In the classical isolations of protactinium,¹⁻³ the starting material was the ultimate residue remaining after extraction of radium following preliminary removal of uranium. These residues were obtained from the Joachimsthal mine in Czechoslovakia. Since these were residues from extensive chemical treatments, it might be expected that the isolation of protactinium from them might be beset with difficulties in addition to those resulting from the chemical nature of the protactinium. Therefore it was considered highly worth while to investigate a less refractory source. The carbonate precipitates from the uranium process were chosen since they represented the probable site of any protactinium that might have dissolved in the original acid treatment and since they had already been in solution and were expected to be amenable to redissolution with simple acid treatment. The ionium content of this fraction similarly would be more readily isolated than that in the original ore or the radium residues. As has already been stated, another possible source of ionium is the residue of the ether extraction procedure.

The analyses of these fractions, to be reported in this paper, show that the carbonate fraction is indeed a relatively rich and readily worked source of both protactinium and ionium and that the ether extraction residues contain ionium essentially free of protactinium or polonium. Their ionium content is something over 6 ppm. The data further show that more than half the protactinium and ionium may be dissolved in the initial acid treatment of the ore and appear in the carbonate fraction.

2. EXPERIMENTAL WORK

Several analytical procedures for determination of protactinium in ores which made use of coprecipitation have been reported in the literature. One procedure, first employed by Hahn and Meitner and developed further by Wildish,⁴ makes use of tantalic oxide as a carrier for protactinium. Another procedure developed by several workers has involved coprecipitation with titanium, especially by hydrolysis of the hydroxide from salts such as the sulfate. Von Grosse¹ has pointed out the inadequacy of tantalum carrier and has suggested instead the use of zirconium phosphate. Through dissolution of this precipitate in hydrofluoric acid, precipitations of carriers for contaminating radioactivities can be made to give radiochemical purification of the protactinium. A manganese dioxide carrier has also been used.⁵ Work in the Manhattan Project laboratories showed further the usefulness of thorium and zirconium iodates and other precipitates which can be used in special circumstances.⁶

The principal long-lived alpha activities present in the fractions examined (excluding the uranium isotopes) are radium, polonium, ionium, and protactinium. The polonium, short-lived in comparison to the others, is still of appreciable half life (140 days) and is supported by its long-lived parent lead isotope RaD (22 years). Radiochemical analytical procedures must therefore be capable of distinguishing these four isotopes where they occur together and of always distinguishing the last three.

The procedures finally adopted depend primarily on the following behavior of trace concentrations of the activities in question:

1. Barium sulfate will carry radium quantitatively, but it will not carry protactinium; thorium isotopes are partially carried.
2. Zirconium phosphate will carry protactinium (and thorium) well under the proper conditions and will not carry radium.
3. Manganese dioxide formed in situ from manganous ion and permanganate will carry polonium quantitatively in both the presence and absence of fluoride.

4. Manganese dioxide will carry protactinium except in the presence of fluoride.

5. When Th^{232} is added to a detectable concentration, manganese dioxide carries no significant amount of ionium activity.

6. When thorium is precipitated with hydrofluoric acid (thereby precipitating the isotopic ionium), neither protactinium nor polonium is carried appreciably.

7. A silver wire will collect polonium from a halogen acid solution.

Three types of residues have been analyzed so far. These consist of the carbonate fraction discussed earlier (three samples), the ultimate sulfate residue mentioned (one sample), and the residue of ether extraction (one sample).

2.1 Carbonate Residues. These consisted of two samples from one process and a third sample from a process operated by a different producer. Treatment with concentrated nitric acid yielded a gelatinous residuum composed mainly of silica; the readily soluble portion and the residue were analyzed separately.

Following separation by centrifugation the gel was treated with HF and perchloric acid. The perchloric acid was eventually fumed off, and the remaining solid matter fused with alkali carbonate. The carbonate melt was leached with hot KOH solution (0.05M) to remove any tantalum present, and the leaches were discarded. The remaining solid was dissolved by fusing it with KHSO_4 and dissolving it in normal HCl. After the addition of some Pa^{233} to act as tracer for the protactinium, radiochemical analysis was carried out.

2.2 Sulfate Residues. The solid material was fused with NaOH and the melt was leached with dilute hydrochloric acid, dissolving about 18 per cent of the solids. This solution was analyzed separately. The remaining solids were fused with carbonate, and the melt was leached with water which was discarded. The solid carbonates then dissolved completely in dilute HCl. Following addition of Pa^{233} tracer the two solutions were analyzed separately.

2.3 Ether Residues. A uniform sample was dried and then fused with carbonate. A water leach of the melt was discarded. The residue was treated with HF and HNO_3 several times and evaporated to dryness each time. Following a final evaporation the material was dissolved in HNO_3 , leaving a white granular residue insoluble in HNO_3 or HF (probably alkaline-earth fluoride). The acid solution was analyzed further. Unfortunately the fluoride residue, which may have been composed in part of thorium fluorides, was discarded. Another analysis, carried out subsequently by C. C. Bard, gave complete solution. The value from this analysis is found in Table 1.

2.4 Analytical Results. A summary of the analytical findings for the residue samples investigated is found in Table 1. The exact values of the analyses are not significant and should be considered only as an indication of relative orders of magnitude. This is necessitated in part by analytical uncertainties and in part by the inhomogeneity of the material itself. The variability from the latter standpoint is necessarily quite large. Decay of polonium is another source of variability. Material balances are not complete, as can be seen. This is due in part to analytical failures and in part to radioactivities other than those being reported (short-lived activities and, in the case of sample 5, radium and its daughters).

The carbonate fractions are seen to contain on the order of 0.3 to 0.35 ppm of protactinium, which is mainly bound with the acid-insoluble siliceous portion of this fraction. The ionium, present to some 15 to 20 ppm, is found in the readily soluble portion of the fraction. Information furnished about the carbonate fraction⁸ is that it is 215 parts out of 580 parts by weight of the crude ore, i.e., 37 per cent. For pitchblende which is 65 per cent U_3O_8 by weight, this indicates that on the order of two-thirds the original protactinium content of the ore was dissolved in the sulfuric acid-nitric acid treatment and precipitated by the carbonate treatment with more than three-fourths of the ionium content following the same path. The apparent high level of ionium in the sulfate residues is in part at least a reflection of the fact that much of the soluble portion of the ore has been removed, giving a bulk concentration. For example, removal of the uranium alone increases the concentration about threefold. It is interesting to note that the radioactivity surviving to the ether residues is practically entirely ionium (together with a certain amount of uranium). It is difficult to assign a concentration factor for this material, but it must be rather large owing to the previous treatments.

On the basis of the results obtained a number of milligrams of protactinium and approximately 0.5 g of ionium (with three times as much Th^{232}) have been obtained in pure state, from a carbonate fraction.⁷⁻⁹ The yields obtained for the protactinium corresponded to 50 to 60 per cent of the material indicated by preliminary analysis. No attempt was made to obtain complete recovery of ionium.

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Table 1 — Analyses of Radioactivity in Uranium-process Residues

Sample origin	Fraction	Total alpha activity at 50 %, c/min/g	Protactinium		Ionium		Polonium	
			% of activity	Ppm	% of activity	Ppm	% of activity	Micro- curie/g
1. Carbonate precipitate from 65% African pitch- blende No. 3-1	HNO ₃ sol.	4.5×10^5	<0.3	<0.03	78	16	20	0.08
	Siliceous residue	3.5×10^6	40	0.27	<20	<0.3	25	0.008
2. As above, but another shipment, No. 3-2	HNO ₃ sol.	2.2×10^4	<1	<0.04				
	Siliceous residue	2.4×10^4	75	0.35	<5	<0.05	20	0.004
3. As above, but from another pro- cessor, No. 7	HNO ₃ sol.	4.4×10^5			≤94	≤19	4-6	0.02
	Gelatinous residue	7×10^4	25	0.38	10	0.3	>50	>0.03
4. Sulfate residue, 65% African pitch- blende, No. 1	Sol. HCl af- ter NaOH	6.0×10^5	≤3.6	≤0.4	90	24	0-5	0-0.03
	Sol. HCl af- ter Na ₂ CO ₃	2×10^6	<0.2	<0.08	5-10	5-9	0-5	0-0.1
5. Residue of ether extraction of uranium, No. 8	HNO ₃ -HF soluble Insoluble fluoride*	1.4×10^5	<0.05	<0.01	~100	6		

*Not Analyzed.

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Paper 6.2

EXTRACTION OF PROTACTINIUM FROM CARBONATE- INSOLUBLE RESIDUES OF URANIUM ORES. I. ISOLATION AND PURIFICATION OF PROTACTINIUM USING HF

By Kurt A. Kraus and Q. Van Winkle

[Editor's Note: This paper is based on Report CC-3365 (Feb. 26, 1946) and covers work carried out in the winter of 1944-1945 at the Metallurgical Laboratory of the University of Chicago.]

ABSTRACT

A method of isolation of milligram amounts of protactinium (Pa^{231}) from a uranium ore residue was developed and is described in detail.

1. INTRODUCTION

The work reported here was undertaken for the purpose of isolating a small amount of protactinium (Pa^{231}), an alpha emitter with a half life of about 32,000 years.¹

Following a suggestion by Katzin² a "carbonate residue" was used as raw material for the isolation, since this material combined a reasonably high protactinium content with fair solubility, as was shown by Katzin, Van Winkle, and Sedlet.³ This carbonate residue is formed in the processing of uranium ores when nitric acid-sulfuric acid extracts of the ore are treated with sodium carbonate. In this procedure advantage is taken of the solubility of uranium in alkaline solutions as the carbonate complex. Since the initial treatment of the ore involves the use of sulfuric acid, the radium content of the carbonate precipitate is low. The laboratory had been advised that, during the acid treatment of the ore, approximately one-third the protactinium would go into solution.⁴ Katzin, Van Winkle, and Sedlet showed that in the carbonate treatment the protactinium is carried by the carbonate precipitate and, since this precipitate contains material which once was

in solution, re-solution for isolation purposes would only be a minor problem. Thus the use of this residue appeared to be a great improvement over the use of the "Ruckruckstande" which served as raw material in previous large-scale isolations of this element,^{5,6} since these residues consist, in essence, of the most insoluble materials in the ore, being the residues which remain after nitric and sulfuric acid treatment of the ore and after radium removal.

The isolation procedure for protactinium which was used by Von Grosse⁵ appeared to be unduly cumbersome since it involved a large-scale sodium hydroxide fusion, repeated zirconium phosphate precipitations followed by potassium carbonate fusions, bisulfate fusions, and fractional crystallization of the chlorides of zirconium and protactinium. It was hoped to develop a flow sheet where the use of zirconium phosphate could be avoided. Furthermore, fusions of sodium hydroxide with large quantities of material seemed to be very undesirable and necessitated the use of equipment which was not immediately available in the laboratory. In addition, it appeared advantageous to apply to this problem the studies on the extraction of protactinium by organic solvents which were under way at the Metallurgical Laboratory.⁷

In preliminary work, difficulties were encountered in the analysis for protactinium. An assay of the total alpha activity present was indecisive, since approximately 95 per cent of the alpha activity of the carbonate residue was due to polonium and ionium which can be distinguished from protactinium only through differences in their respective ranges. [Using a sensitive instrument such as a "pulse analyzer" for range measurements, the difference in ranges can readily be used for analytical purposes. Such an instrument was not available when this work was carried out.] In the absence of a sensitive instrument for range measurements a chemical separation of protactinium from other alpha emitters was necessary before an alpha assay for protactinium could be carried out. Unfortunately, the chemical separations⁸ (e.g., with manganese dioxide or zirconium phosphate as carriers for protactinium) were not always clean-cut. In several instances manganese dioxide and zirconium phosphate failed entirely to coprecipitate protactinium. In view of these difficulties a tracer solution of Pa^{233} (a beta emitter with a half life of 27.4 days) was added to the solutions in large enough quantity to permit substitution of beta assaying for most analyses for Pa^{231} during the isolation.

2. SUMMARY OF ISOLATION PROCEDURE

The main steps in the isolation of protactinium from the carbonate residue were the following:

1. The carbonate residue was treated with an excess of nitric acid which dissolved approximately 80 per cent of the solid material and left 95 per cent of the protactinium in the insoluble residue. Approximately 90 per cent of the ionium and polonium went into solution.

2. The washed residue from the nitric acid treatment was treated with hydrofluoric acid in the presence of sulfuric acid at elevated temperature. During this treatment over 90 per cent of the protactinium went into solution while (with the particular residue used here) only a small proportion of the bulk of the residue dissolved.

3. The hydrogen fluoride and fluosilicic acid (from silica in the residue) were removed from the solution by fuming (not to dryness) with sulfuric acid. Some solid material which separated during this process could be readily dissolved by dilution with 2M HNO_3 .

4. Manganese dioxide was precipitated from this solution to carry the protactinium. The MnO_2 carried practically all the polonium activity but less than 10 per cent of the protactinium. The reason for the failure of manganese dioxide to carry protactinium is not clear; it is possible, however, that some residual fluoride ions may have inhibited the carrying. Carrying of protactinium from this solution by zirconium iodate was successful.

5. Concentration of protactinium with respect to zirconium was achieved by first fractionally dissolving zirconium iodate with an appropriate reducing agent, leaving the protactinium with the residual undissolved zirconium iodate. Using hydroxylamine nitrate and nitric acid, 70 per cent of the original zirconium iodate was dissolved, while 95 per cent of the protactinium remained with the undissolved zirconium iodate fraction. The remaining precipitate was then completely dissolved with hydroxylamine nitrate and nitric acid. The protactinium was removed from this solution by partially precipitating the zirconium iodate.

6. Protactinium was separated from zirconium (and other impurities) in the above solution by solvent extraction, using diisopropyl ketone. Four cycles were used, with each cycle consisting of (a) extraction of protactinium into ketone from 8N HNO_3 , (b) extraction of protactinium from the ketone by 0.1M oxalic acid, and (c) destruction of the oxalic acid with diammoniumhexanitratocerate.

7. Final purification was carried out by precipitating protactinium as a peroxide, dissolving the peroxide in hydrochloric acid, and extracting the protactinium with diisopropyl ketone from the hydrochloric acid solution.

3. DETAILS OF ISOLATION AND PURIFICATION

3.1 Bulk Reduction with HNO_3 . Six kilograms of carbonate residue were treated with 12 liters of concentrated nitric acid after wetting with 3 liters of water. After gas evolution had ceased, the suspension was heated for 12 hr. After cooling, hydrogen peroxide was added to dissolve any MnO_2 which was present.

This procedure was used mainly to achieve bulk reduction. Eighty per cent of the material went into the nitric acid solution together with a considerable amount of alpha and beta activity (3×10^8 alpha dis/min and 7.5×10^7 beta dis/min/kg of carbonate residue). However, practically no Pa went into the solution, the alpha activity being due mainly to polonium and ionium.

3.2 HF Leaching. The nitric acid insoluble residue was transferred to two 1-liter platinum dishes and treated with hydrogen fluoride in the presence of 200 ml of concentrated sulfuric acid. After digestion at elevated temperature for approximately 48 hr, the HF solution was separated from the insoluble material and was found to contain 2.2×10^8 alpha dis/min and 3.5×10^6 beta dis/min/kg of carbonate residue used. The total volume of the $\text{HF-H}_2\text{SO}_4$ solution was 3.4 liters. A second leach with HF in the presence of 150 ml of concentrated sulfuric acid was carried out (with a 48-hr digestion period) from which 2.4 liters of fluoride solution was obtained containing 5.5×10^6 alpha dis/min and 2.4×10^5 beta dis/min/kg of carbonate residue. The remaining residues (400 g) still contained 16×10^6 alpha dis/min but not more than a total of 80 μg of Pa. This residue was assayed by potassium acid sulfate fusion and dissolution of the melt in dilute HNO_3 . From a portion of the resulting solution, zirconium phosphate was precipitated in the presence of Pa^{233} tracer. The precipitate was then assayed for Pa by range measurements with mica absorbers.

3.3 Removal of HF. There are indications^{8,9} that in the presence of sulfuric acid protactinium can be heated safely with HF without loss through volatile fluorides. A number of further tests were carried out, showing that the same holds true for the HF solution under consideration. The hydrogen fluoride was removed by evaporating the HF solution in the presence of sulfuric acid and allowing the sulfuric acid to fume for some time. A considerable amount of materials separated during this process, most of which could be redissolved by treating the small remaining volume of sulfuric acid with dilute nitric acid. The resulting 2M HNO_3 solution had a volume of 1100 ml. Less than 1 g of insoluble and inactive material was left behind.

3.4 Precipitation of MnO_2 . It was originally contemplated to carry the protactinium from this nitric acid solution by the use of MnO_2 , which had previously been shown to be a good carrier for Pa (references 10-12). Two successive precipitations were carried out, the first one carrying approximately 50 per cent of the alpha activity and the second one carrying another 10 per cent. The MnO_2 precipitates were worked up extensively, but finally it was shown that they did not contain more than 10 per cent of the total amount of Pa in the solutions. The reason for the failure of MnO_2 to carry is not understood. It is possible (though unlikely, in view of the prolonged fuming) that a residual amount of fluoride remained in the solutions and inhibited the carrying. [The possible interference of sulfate ions with carrying was not investigated.] The MnO_2 (1 mg/ml) precipitations were carried out at elevated temperatures (100°C water bath) by first adding a three-fold excess of manganous ions and then slowly adding the calculated amount of potassium permanganate solution.

The MnO_2 was first dissolved with hydrogen peroxide in the presence of dilute HNO_3 . Such treatment, however, was found to be undesirable, since it lead to insoluble materials, which had to be fused to make them soluble once again. When hydroxylamine was used for dissolving MnO_2 precipitates, no insoluble residues were obtained. The insoluble precipitates were not analyzed but probably contained some of the elements of the fourth and fifth row of the periodic table. These are probably mainly zirconium, niobium, tantalum, and titanium, which was found to be a very persistent impurity in spite of the fact that it forms a soluble peroxy acid. Much less difficulty was encountered in the removal of vanadium with peroxide.

The MnO_2 precipitations were carried out hot, and this is probably the reason why so many of the ions mentioned above were present. They were probably hydrolyzed during the heating process to give the insoluble acids. If Pa is to be carried by MnO_2 , precipitations at room temperature appear preferable since such precipitates were later generally found to carry Pa as well as precipitates formed at elevated temperatures.

3.5 Zirconium Iodate Carrying. After the failure of MnO_2 to carry, sufficient Pa^{233} tracer was added to the solution to make it the predominant beta emitter. An additional small-scale test on the carrying by MnO_2 confirmed the previous results; less than 10 per cent of the beta tracer was carried. A test of the extractability of the protactinium with diisopropyl ketone also failed. However, zirconium iodate previously introduced as a carrier for Pa (reference 11) was found to carry 98 per cent of the Pa^{233} tracer together with approximately 95 per cent of the alpha activity of the solution. The zirconium iodate

precipitated from the solution only after the iodic acid concentration exceeded about 0.15M. The final precipitation was carried out from 0.3M iodic acid.

3.6 Self-concentration of Protactinium on Zirconium Iodate. Zirconium iodate can be readily dissolved by the addition of appropriate reducing agents such as iodide ions or hydroxylamine. When the work was carried out, it was planned to solvent extract the resulting solution. Since this procedure had been worked out only for nitrate solutions at that time, hydroxylamine nitrate [prepared from hydroxylamine chloride with silver nitrate and hydroxylamine sulfate with a slight excess of barium nitrate] was used for dissolving the iodate. Reduction with iodide was not attempted, since the amount of iodine liberated would have been very much larger than with hydroxylamine.

The iodine which resulted from the reduction of the iodate was removed by extraction with toluene.

After approximately 70 per cent of the zirconium iodate had been dissolved with hydroxylamine without dissolving an appreciable amount of protactinium, the supernatant was removed by centrifugation. The residual zirconium iodate was dissolved, yielding a solution whose volume was only 1 per cent of the volume of nitric acid solution from which the iodate was precipitated.

Iodic acid was added slowly to the zirconium-Pa solution until 95 per cent of the protactinium had been carried; this was achieved when approximately 30 per cent of the zirconium had precipitated. The resulting zirconium iodate was removed by centrifugation and dissolved in hydroxylamine nitrate in the presence of 1M HNO_3 to yield a clear solution of approximately 2 ml volume. The zirconium iodate precipitation therefore affords an exceedingly potent method for volume reduction and yields readily soluble precipitates (e.g., niobium, tantalum, and zirconium do not become insoluble). Its use thus eliminates cumbersome fusions.

3.7 Solvent Extraction with Diisopropyl Ketone. Solvent extraction with diisopropyl ketone has been found⁷ to be exceedingly efficient and to permit extraction of 70 per cent of the protactinium from approximately 2M nitric acid in one equilibration with an equal volume of ketone in the absence of any other salting-out agents. [For some tests on the extractability of zirconium, see Sec. 5.] Tests on the final solution described in Sec. 3.6, however, showed that not more than 15 per cent of the protactinium could be extracted under these conditions with an equal volume of ketone. It is very unlikely that enough fluoride or sulfate ions could have been present to inhibit extraction, since all precipitates had been washed thoroughly.

With micro experiments it was found that an increase in the nitric acid concentrations of the solutions raised the extraction efficiency to 20 per cent for equal volumes of solvent and solution. When the main volume of the solution was worked up, the increase in nitric acid concentration caused fairly violent reaction with the excess hydroxylamine present and caused the solution to heat up considerably. The efficiency of extraction dropped to 3 per cent. It is believed that the heating of the solution was responsible for this drop in the efficiency of the extraction.

It is highly probable that this low extractability of protactinium is due to a hydrolytic polymerization (formation of colloidal hydroxide). Such polymerization would be expected to occur more readily in a more concentrated protactinium solution (the solution in question had a concentration of 0.2 mg Pa/ml), and thus tracer experiments could very easily differ considerably from experiments carried out at high concentration. A further indication that the low extractability is due to polymerization is that heating decreases the extractability since hydrolytic polymerization would also be expected to increase with heating.

By adding large quantities of zirconium nitrate and nitric acid it was possible to raise the efficiency of extraction to 15 per cent per equilibration with an equal volume of solvent. Only about 75 per cent of the protactinium was extracted in this way (using a total of 200 ml of solvent), since the efficiency of extraction tended to decrease continuously.

To avoid an excessive increase in the volume of the solutions during the stripping of the solvent with an aqueous solution, the extraction of the solvent was carried out with 0.1M oxalic acid rather than with water. Before reextraction of the aqueous layer with diisopropyl ketone, the oxalic acid in the aqueous layer was first oxidized with ceric ions $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$, the solid ceric salt being added slowly to the solution until the reaction was complete, as evidenced by a permanent coloration of the solution.

No exact data regarding the distribution coefficients for the later equilibrations can be given. Data for better controlled experiments can be found in a separate paper.¹³ The following qualitative observations were made:

During the equilibration of the ketone with a strongly acidic solution, a very considerable proportion of the acid is extracted into the solvent phase, as had been demonstrated by Wolf.⁷ The first ketone extraction of the solution was made from an aqueous layer which had been made approximately 8M in nitric acid in an attempt to increase the abnormally low extraction of the Pa. The acid concentration of

the ketone layer must therefore have been very high. This acid appeared to reextract into the aqueous phase during the stripping of the solvent with the result that, even in the presence of oxalic acid, the distribution coefficient was such as to leave most of the protactinium in the ketone layer. After a sufficient decrease of the acid concentration is achieved through successive equilibration with the aqueous phase, the distribution coefficient changes rapidly, and the bulk of the protactinium can be collected in a very small volume of oxalic acid solution (5 to 10 per cent of the ketone volume). Thus theoretically the volume reduction for an extraction cycle using oxalic acid and ceric ions (for oxidation) should be very high (fivefold or higher), but it is usually lower because of the high acid concentration of the starting solution. During the first extraction cycle, for instance, a volume reduction by a factor of only 2.5 was obtained. This factor increased to 4 during later extraction cycles. A consideration of the distribution coefficients for nitric acid solutions and nitric acid-oxalic acid mixtures leads to the theory that the optimum concentration (for maximum volume reduction) of the nitric acid in the aqueous phase is near 2M HNO_3 .

A total of four extraction cycles was carried out. During the later cycles losses appeared which in the fourth cycle (where the volume had again been reduced to about 5 ml) amounted to approximately 50 per cent of the protactinium present. After it was ascertained that the difficulty was due to the deposition of protactinium on the walls of the vessels, the extraction was stopped.

This deposition of protactinium on the walls of the vessel may be due either to the precipitation of protactinium oxalate (which is reported to be insoluble)¹⁴ or to hydrolysis of protactinium in the nitric acid solution.

3.8 Further Purifications. The protactinium which had deposited on the walls of the containing vessel was collected through the use of hydrogen fluoride, and the resulting solution was brought to a small volume (less than 0.1 ml) by evaporation in a small platinum dish and fuming in the presence of perchloric acid. During this procedure the protactinium precipitated out, and all attempts to dissolve this residue in nitric acid (including concentrated nitric acid) failed.

The insolubility of the protactinium at this stage was at first attributed to a possible "meta acid" formation on heating. The insoluble and refractory material was readily soluble in hydrofluoric acid, and an attempt was made to crystallize the ammonium fluoride double salt from the solution. This double salt would be expected to be soluble in nitric acid, and the difficulties due to a meta acid should have been circumvented. At this stage in the purification a further solvent

extraction was planned which would necessitate the removal of fluoride ions. For this reason in two attempts H_3BO_3 and $\text{Al}(\text{NO}_3)_3$, respectively, were added in rather large quantities to complex excess fluoride ions. In the mixture of complexing agent and nitric acid the fluoride was at first soluble, and it was possible to begin a solvent extraction. However, after a very short period of time, of the order of a minute, most of the protactinium precipitated from the nitric acid solution, making it impracticable to carry on further solvent extractions. This precipitation almost certainly was due to hydrolysis, Pa apparently not being sufficiently complexed by nitric acid to prevent it.

In view of this great insolubility of protactinium in relatively concentrated nitric acid, further attempts at solvent extraction were made from hydrochloric acid solutions instead. However, it developed that even concentrated HCl is only a fair solvent for protactinium. From early experiments it appeared that not more than about 300 mg/ml dissolved at room temperature. At elevated temperature this solubility appeared to increase, solutions containing at least 500 mg/ml having been obtained. This change in solubility with temperature for protactinium in HCl solution appeared to be reversible. Thus it appears very doubtful that the limited solubility in HCl solution is due to hydrolysis of Pa to the hydroxide, since, for these elements in general, increase in temperature makes the hydroxide more insoluble rather than more soluble and the reactions are generally not reversible. This difference in the hydrolytic properties of Pa in HCl and HNO_3 solutions must be due to complexing of Pa by chloride ion. A further indication that in HCl solutions extensive hydrolysis of Pa is inhibited is that solvent extraction of Pa from the HCl solutions was fairly successful even at high Pa concentrations.

While the material was prepared for its final solvent extraction, it was necessary to collect it several times by means of hydroxide precipitations. These precipitations were carried out in excess ammonia at room temperature, and the "solubility" of protactinium under these conditions was surprisingly high. Ammoniacal supernatants containing as much as 50 to 100 mg of Pa per liter were observed. Von Grosse¹⁵ reported that protactinium can be quantitatively precipitated from basic solutions after heating. Thus our observations involving solubilities at room temperature are not necessarily at variance with his observations.

The final isolation of protactinium was thus very much complicated by the difficult hydrolytic behavior of protactinium, a behavior which is much more similar to tantalum as commonly stated in the literature^{16,17} than to neptunium(V) and plutonium(V). With these latter ions no difficulties occur in preparing fairly concentrated solutions even in

dilute nitric acid or hydrochloric acid solutions. This difference in the behavior of these various ions of oxidation number five therefore suggests fundamental differences in the structure of these ions in solution.

3.9 Final Isolation and Purity of Protactinium. Final purification of the protactinium was carried out by solvent extraction by diisopropyl ketone from concentrated hydrochloric acid solution. No data are available regarding the purity of the protactinium at this step. However, a small amount of titanium seemed to be present, as indicated by a yellow coloration on addition of peroxide. The extractions were quite efficient, usually more than 70 per cent of the protactinium being extracted by an equal volume of solvent. An attempted stripping of the solvent with 5 per cent hydrogen peroxide in aqueous solution failed, owing to the apparently high solubility of the peroxide in diisopropyl ketone in the presence of high concentrations of HCl. To separate the protactinium from the solvent, the solvent layer was equilibrated with an ammoniacal water solution. The resulting protactinium was radiochemically and chemically pure except for a contamination of about 0.75 per cent of zirconium.

4. CONCLUSION

The method developed for the isolation of protactinium from the carbonate residue of uranium ores appears to be considerably less cumbersome than other methods described in the literature. It was found possible to isolate protactinium without going through any salt fusions or sodium hydroxide fusions. The method of isolation, as finally developed, involves relatively few steps: (1) bulk reduction of the carbonate residue by nitric acid treatment, (2) HF leach of the residue, (3) removal of the resulting HF by fuming, (4) carrying and volume reduction by zirconium iodate, and (5) solvent extraction with diisopropyl ketone. The purity of the material obtained in this way seems to be satisfactory, both radiochemically and chemically.

The choice of the carbonate residue as the starting material in the isolation of protactinium should be considered seriously in spite of the fact that those carbonate residues which have been studied did not contain a much larger concentration of protactinium than the original ore (1 kg of uranium contains approximately 0.3 mg of protactinium). The main advantage in using the carbonate residue for the isolation results from the relative ease of dissolving it and from the absence of radium. A number of different carbonate residues have been analyzed; and the concentration of protactinium appears to vary considerably, though not as much as the total alpha activity. Using four different residues (whose source could not be established), the following assays were obtained in this laboratory:

Total alpha activity, dis/min/kg $\times 10^8$	10	8	4	3
Conductivity of Pa, ppm	0.3	0.26	0.22	0.3

Practically no analyses have been carried out for impurities throughout the whole isolation procedure. The relative merit of the various steps is therefore in doubt. Nevertheless, various impurities have been identified or tentatively identified during the isolation from qualitative considerations. Thus, for instance, it was shown that a small amount of titanium carried through to practically the last extraction, since a peroxide solution of protactinium showed the typically yellow color of titanium.

During the isolation an MnO_2 precipitation had been carried out, which was later shown to be unnecessary. The MnO_2 precipitations, however, may have contributed very greatly to the final purity of the protactinium isolated, since a large amount of titanium and vanadium, for example, coprecipitated with it. Furthermore, the manganese dioxide precipitates must have carried practically all the polonium in the solution and probably also the ionium. This becomes clear if it is borne in mind that the bulk of the alpha activity was carried along with the manganese dioxide and that in the next step, the zirconium iodate precipitation, practically all the residual alpha activity was carried together with practically all the beta activity (Pa^{233} tracer) of the solution. Since, from this step on, the ratio of alpha and beta activities was practically constant (after correction for decay of Pa^{233}), the conclusion could be reached that any ionium that might have been present was carried by manganese dioxide although it appears more probable that any ionium which was not dissolved in the initial HNO_3 treatment of the ore residue was retained by the residue during the fluoride treatment, at which time it was probably carried by the insoluble fluorides.

If, as is suggested, the isolation of protactinium is carried out without a manganese dioxide precipitation, polonium (and perhaps ionium) would be expected to be present at the time the zirconium iodate is precipitated. Probably both these alpha emitters would be at least partially carried by the zirconium iodate, and the main responsibility for purification would fall on the solvent-extraction step. In view of the great solubility of protactinium in the solvent at relatively low acid concentrations, no difficulties would be expected from ionium. Polonium in the presence of nitric acid would still be somewhat extracted, together with the protactinium. However, it could then be separated by washing the solvent layer with about 1M nitric acid.¹⁸ During this washing relatively little protactinium would be lost, provided the acidity of the solution was not permitted to drop to too low a value. Furthermore, polonium could usually be readily removed

from HCl solutions by inserting a silver strip and permitting the solutions to stand overnight.

The general method of isolation of protactinium will more or less depend on the success of the solvent extraction. Although in the isolation described here difficulties were encountered in the solvent-extraction step owing to the special hydrolytic properties of protactinium, the use of solvent extraction still appears to be feasible even with macro (rather than tracer) concentrations of protactinium if HCl, rather than HNO_3 , solutions are used.

5. SOLVENT EXTRACTION OF POLONIUM, ZIRCONIUM, AND NIOBIUM BY DIISOPROPYL KETONE

The following experiments were carried out to test the usefulness of solvent extraction by diisopropyl ketone in the purification of protactinium from polonium, zirconium, and niobium. It was found that the extractability of zirconium and niobium is small enough to permit their separation from protactinium. Furthermore, it was found by solvent extraction that polonium can, under certain conditions, extract to a very large extent from HCl solutions. An appreciable extraction was also found for polonium in a nitric acid solution.

5.1 Polonium. (a) Nitric Acid Solutions. A Po^{210} tracer solution in nitric acid (1M HNO_3) was equilibrated with an equal volume of diisopropyl ketone, using as a salting-out agent 1M $\text{Mn}(\text{NO}_3)_2$. The ketone layer contained 7 per cent of the polonium.

(b) Hydrochloric Acid Solutions. A Po^{210} tracer was extracted from 3M, 6M, and 9M hydrochloric acid solutions without the addition of further salting-out agents by equilibration with equal volumes of diisopropyl ketone. The results are summarized in Table 1.

Such very large extractability of polonium from HCl solutions might be very useful in the isolation of polonium from other materials, although of course it means that no purification of protactinium with respect to polonium can be expected by solvent extraction with diisopropyl ketone.

The different result obtained with 1M HNO_3 may easily have been due to the lower concentration of acid, although a further investigation of nitric acid solutions would be in order.

5.2 Zirconium and Niobium. Only a mixed tracer solution of zirconium⁹⁵ and niobium⁹⁵ was available for the tests, containing approximately equal activities of zirconium and niobium. The extractions were carried out from 3M, 6M, and 9M HCl solutions by equilibration with equal volumes of diisopropyl ketone. The results are summarized in Table 2.

From this table it may be seen that up to 6M HCl the extractability of either zirconium or niobium is negligible and that therefore purification from both zirconium and niobium can be expected by solvent extraction with diisopropyl ketone from HCl solutions.

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Table 1—Extraction of Polonium from HCl Solutions

Initial conc. HCl, molarity	3.0	6.0	9.0
Po extracted into ketone, %	69	95	98

Table 2—Extraction of Mixed Zr⁹⁵-Nb⁹⁵ Tracer from HCl Solutions

Initial conc. HCl, molarity	3.0	6.0	9.0
Mixed tracer extracted into ketone layer, %	0.3	1.3	10

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Paper 6.3

EXTRACTION OF PROTACTINIUM FROM CARBONATE-INSOLUBLE RESIDUES OF URANIUM ORES. II. "GEL PROCEDURE" FOR ISOLATION OF PROTACTINIUM

By Raymond G. Larson, Leonard I. Katzin, and Eugene Hausman

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1. INTRODUCTION

Isolations have been made of protactinium (Pa^{231}) from the ultimate residues of uranium ore processed for recovery of radium.¹⁻³ This material is highly refractory and difficult to work. Katzin, Van Winkle, and Sedlet⁴ have shown that this starting material is a relatively poor one from the standpoint of protactinium content and that the first carbonate precipitate in the recovery of uranium from pitchblende ores is a better source of the protactinium. In this carbonate material, which is relatively readily soluble (having once been in solution), the protactinium is present to some 0.2 ppm. A small-scale isolation of protactinium from this source by Kraus and Van Winkle⁵ has been made in which an important step is reduction of the silica content by evaporation with hydrofluoric acid. For large-scale work, this sort of procedure and large-scale fusions, such as Von Grosse^{1,2} and Graue and Kaeding³ were forced into, are to be avoided. With the process to be described in this paper bulk reduction is achieved by leaching the soluble nitrates from the silica gel which forms in the material and to which the protactinium adheres. The silica is destroyed by aqueous alkali, and the protactinium is concentrated and purified by solvent extraction.⁶

2. EXPERIMENTAL WORK

The nature and previous history of the carbonate residue used as starting material have been described before.⁴ Preliminary experi-

ments showed that treatment of the carbonate residue with strong nitric acid left a gel after the neutralization was completed. After thorough leaching with nitric acid, the gel was treated with hydrofluoric acid and shown to dissolve completely, indicating that it was silicic acid. The large bulk of the protactinium alpha activity was found to have remained with the silicic gel, rather than to have been extracted by the leaching process.

On the basis of this observation a more detailed study was made of the effects of different variations of the procedure, on the basis of which the following assay method for the Pa^{231} content of the carbonate residue was evolved. The sample of carbonate residue was treated with Pa^{233} tracer solution and nitric acid to form a slushy gel. After leaching the gel with dilute nitric acid until 99 per cent of the dissolved-solids content was removed, carrier amounts of lanthanum nitrate were stirred into the gel. The gel was then destroyed with sodium hydroxide leaving a residue about 5 per cent or less of the bulk of the gel. The lanthanum hydroxide formed served as a carrier for the precipitated protactinium. The separated solid was redissolved with dilute nitric acid at ice-bath temperatures, and the solution was extracted with diisopropyl ketone. A portion of the ketone extract was then mounted for determination of alpha and beta activity. A range analysis for identification of the alpha activity was made with the aid of the differential pulse analyzer.

Using the value for the protactinium content of the ketone extract so obtained and correcting the extraction value by the distribution of the Pa^{233} tracer, it is possible to estimate a value for the protactinium content of the original residue. Assuming the loss of protactinium in the leaching processes and other treatments is given by the loss of Pa^{233} tracer, the content may be as high as 0.24 ppm in the carbonate material (two analyses of 10-g samples). However, it is certain that exchange between the protactinium isotopes in the early stages of the procedure is poor, so the amounts of Pa^{231} lost may be much less than the tracer indicates. The value 0.2 ppm is probably fairly representative. The alpha and beta activities of the original carbonate residue were about 2×10^5 and 2×10^4 c/min/g, respectively. The Pa^{231} alpha activity was probably about 5 per cent of the total, based on the above-mentioned analysis. The other alpha activity was largely ionium, with some polonium also present.⁴

The semiworks flow sheet which evolved from these findings was essentially the same as the assay method:

1. With 15 kg of carbonate residue in a stainless steel tank of about 150 liters capacity, stir in 15 liters of distilled water and follow with 18 liters of concentrated nitric acid, added over a period of about

½ hr. The slushy gel which is formed should be allowed to settle for at least 8 hr.

2. Leach the gel five times with two volumes of 1N nitric acid solution. Stir about 1 hr and allow to settle at least 8 hr for each leach. Siphon off clear supernatants.

3. Add 7½ g of lanthanum as the lanthanum ammonium nitrate and stir about 15 min. Add solid sodium hydroxide to a concentration of 10 per cent. The mixture should be stirred for about 1 hr and allowed to settle at least 8 hr. Siphon off the clear supernatant.

4. Slurry the hydroxide residue into a container for transportation to laboratory and further processing there.

The semiworks operations were performed with little difficulty. The dissolving of the carbonate residue was accompanied by some foaming, which caused no trouble. After initial settling of the gel there was only 5 per cent of clear supernatant. The leaching of the gel with 1N nitric acid solution gave slightly cloudy supernatants during the last two or three of the five leaches.

Control assays for Pa^{231} activity were made by two methods. In one, solvent extraction with diisopropyl ketone was used, with Pa^{233} tracer added to estimate the proportion of Pa^{231} being extracted. Uranium and some ionium would also be extracted and thus make results unreliable. The other method was that of precipitating thorium fluoride as a carrier of ionium; the hydrofluoric acid supernatant was then treated with a manganese dioxide precipitate which carries polonium but not protactinium from hydrofluoric acid solutions. The residual alpha activity was ascribed to Pa^{231} . By this method uranium would also be associated with the Pa^{231} activity. It was estimated that perhaps 15 to 50 per cent of Pa^{231} activity was lost in the nitric acid leaches. When cloudy supernatants were obtained, the estimated Pa^{231} loss was in the higher part of this range. It is possible that the actual Pa^{231} was nearer the lower limit, since some uranium alpha activity is present in the solution. No loss of alpha activity occurred in clear alkaline supernatants.

The hydroxide residue from three semiworks runs, representing 45 kg of carbonate residue, was processed in the laboratory as follows: After several washes with 5 per cent sodium hydroxide solution, to obtain more complete removal of residual sodium silicate, the hydroxide residue was leached with 3N nitric acid at ice-bath temperature. The nitric acid leach was then solvent extracted with diisopropyl ketone [distribution coefficients were rather low]. The Pa^{231} was precipitated from the ketone by treating it with sodium hydroxide solution. A small amount of lanthanum hydroxide in the aqueous layer was used as a carrier in this concentration step. The lanthanum hydroxide pre-

precipitate was dissolved with nitric acid at ice-bath temperature and solvent extracted again with diisopropyl ketone. The protactinium hydroxide was this time precipitated from the ketone by addition of excess concentrated ammonia solution.

The hydroxide precipitate was further purified by hydrolysis in 1N nitric acid at hot-water-bath temperature. Four 1N nitric acid leaches of the precipitate were made. The residual protactinium oxide was evaporated to dryness in a platinum dish, treated with concentrated hydrofluoric acid, and again evaporated to dryness. The hydrofluoric acid residue was then dissolved in 6N hydrochloric acid and stored in a wax-lined glass cylinder.

At the time of writing approximately 2 to 3 mg of protactinium has been obtained in relatively pure form. About 0.7 mg is in a repurified HCl solution for which a spectrochemical analysis reported definite impurities of 1.5 per cent iron, 0.15 per cent calcium, and 0.035 per cent magnesium. Another 4 mg of Pa^{231} has been obtained in a less pure condition. This accounts for perhaps 75 per cent of the Pa^{231} expected to be in the carbonate residue worked up.

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Paper 6.4

EXTRACTION OF PROTACTINIUM FROM CARBONATE- INSOLUBLE RESIDUES OF URANIUM ORES. III. MANGANESE DIOXIDE PROCEDURE

By Roy C. Thompson, Q. Van Winkle, and John G. Malm

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ABSTRACT

A procedure is described by means of which 20 mg of protactinium was obtained in pure form from 200 kg of uranium residues. The procedure employs MnO_2 as a coprecipitating agent to secure initial concentration of the protactinium by a factor of about 1000. Final purification is achieved principally by a nonaqueous solvent-extraction technique utilizing diisopropyl ketone.

1. INTRODUCTION

A number of procedures have been described and employed for the isolation of protactinium from natural materials.¹⁻⁵ Except for the procedure described in Paper 6.3, this volume, all these methods suffer the disadvantage of large-scale fusions and/or hydrofluoric acid treatments. They are all quite tedious and usually involve the reworking of many fractions if satisfactory yields are to be obtained. The process to be described in this paper is one which requires, in addition to ordinary laboratory equipment, only a 50-gal tank capable of withstanding the action of 1N nitric acid and equipped with an efficient stirrer. All operations are of the simplest type; large-scale heating, centrifugation, and filtration operations have been avoided. This simplification has been obtained, to a certain extent, at the expense of yield. However, the comparatively readily available start-

ing material employed reduces the importance of yield considerations. It is also true that the performance reported in this paper, indicating a recovery of about 50 per cent of the protactinium originally present, is certainly not the best of which the method is capable. Under the exigencies of wartime pressure, time was not taken to study carefully the factors affecting yield in each step of the process, the rapid attainment of the pure protactinium being of greater interest than the development of the best possible process.

The starting material employed is the carbonate-insoluble material present in the initial solution of pitchblende. This "carbonate residue" has been described in detail as to composition and chemical behavior in preceding papers of this series.⁴⁻⁶ The protactinium content is about 0.2 ppm. Concentration of protactinium is achieved by its coprecipitation with manganese dioxide from a solution of the carbonate residue. This precipitate is dissolved, and the protactinium is again coprecipitated with a smaller amount of manganese dioxide. This procedure is repeated a third time; it results, under the best conditions employed, in about a thousandfold concentration of the protactinium with a 65 per cent yield. After several steps to remove specific impurities the protactinium is isolated and purified using absorption, diisopropyl ketone extraction, and precipitation techniques. The exact sequence of operations is outlined in the concentration flow sheet (Fig. 1) and described in the sections which follow.

2. SOLUTION OF CARBONATE RESIDUE

The carbonate residue contains appreciable quantities of silica. If this residue is dissolved in nitric acid, the resulting solution will eventually set to a semisolid gel unless diluted to impractical volumes. It was found that, by treating the residue with 40 per cent sodium hydroxide, sufficient silica was removed to prevent subsequent gel formation. In large-scale practice this operation was performed in a 40-gal stainless steel tank equipped with a heavy-duty stirrer. Ten kilograms of carbonate residue was charged per batch; 20 liters of water and then 8 kg of solid sodium hydroxide were added. The heat of solution of the sodium hydroxide raised the temperature to about 80°C, and it maintained itself at about 60°C for the duration of the treatment. The thick slurry was stirred intermittently for short periods. Excessive stirring prolonged the subsequent settling time of the metathesized residue. After about 4 hr the slurry was diluted to 100 liters with water and mixed well, and the residue was allowed to settle overnight. The supernatant was withdrawn, and the residue was washed once with water by decantation. The residue was then dissolved by addition of concentrated nitric acid to an

acidity of 1N. A small fraction remains insoluble. The solution is transferred to another tank, and the next charge of carbonate residue is added on top of the insoluble material from the first. Since there was no appreciable build-up of insoluble material in this tank after the processing of over 200 kg of carbonate residue, it may be assumed that essentially all the material is brought into solution after repeated alkali and acid treatments.

The solution which results occupies a volume of about 50 liters. It can be caused to gel only by raising the acidity to about 5N.

3. CONCENTRATION OF PROTACTINIUM

Preliminary coprecipitation tests from carbonate residue solutions indicated that the protactinium present in the process solution was not behaving like protactinium in pure tracer solutions. Thus precipitation of such substances as manganese dioxide⁷ and bismuth phosphate⁸ which carry protactinium quantitatively from pure tracer solutions gave very erratic results varying from no carrying at all to 50 to 60 per cent as a maximum. This sort of behavior has often been encountered with impure protactinium preparations and is quite reminiscent of the behavior of niobium and tantalum in complex mixtures. As has previously been observed,⁵ the carrying of the protactinium is considerably improved by precipitation (along with other alkali-insoluble material present) as the hydroxide, followed by reacidification and separation of the carrier precipitate. Using such a procedure and conducting the alkaline digestion at temperatures of 75 to 100°C, protactinium was carried upon manganese dioxide to the extent of from 75 to 90 per cent.

In the procedure eventually adopted for routine operation, solid sodium hydroxide is added immediately following manganese dioxide precipitation. A rather thick hydroxide slurry is thus obtained which is agitated for 2 to 4 hr. The heat of solution of the sodium hydroxide is sufficient to maintain the mixture at temperatures in excess of 60°C. After the digestion at a hydroxide ion concentration of about 1N, concentrated nitric acid is added to dissolve the hydroxides and to result in a 1N acid solution. The heat evolved during the neutralization aids in the flocculation of the manganese dioxide. Difficulty due to the formation of colloidal manganese dioxide was encountered in the first concentration cycle only when the alkaline slurry was allowed to stand longer than 4 hr and cool to near room temperature. Considerable difficulty with colloidal manganese dioxide was encountered in the second and third cycles. Addition of sulfuric acid to a concentration of 0.1M was found to almost entirely eliminate this occurrence. The first manganese dioxide precipitate was separated

by decantation. The second and third precipitates were small enough to allow centrifugation in 200-ml bottles following initial decantation.

No difficulty was encountered in dissolving the manganese dioxide precipitates if the acid concentration did not fall too far below 1N and if stoichiometric quantities of sodium nitrite were added. A considerable amount of white residue carried down with the manganese dioxide remained insoluble in the sodium nitrite solution. This consisted partly of insoluble sulfates. Spectrographic analysis showed the principal cations in this insoluble residue to be calcium and silicon, with iron, manganese, sodium, barium, tin, titanium, and vanadium also present in significant amounts. The amount of protactinium lost in these residues amounted to about 8 per cent of that originally present in the starting material.

The 1N nitric acid solution of the third manganese dioxide precipitate, upon standing for days or weeks, deposited a gelatinous white precipitate which contained most of the protactinium. This process was accelerated, and the carrying of protactinium was made essentially quantitative by increasing the acidity to about 5N and heating the solution in a boiling-water bath. The precipitate thus obtained was separated, dissolved in concentrated hydrofluoric acid, and fumed to dryness with perchloric acid in a platinum dish. This operation effected the complete removal of silicon which, if allowed to remain even in very small amounts, would have interfered with subsequent solvent-extraction operations.

The residue from the hydrofluoric acid treatment was suspended in a small volume of 10N nitric acid, and an approximately equal volume of 30 per cent hydrogen peroxide solution was added slowly with warming and stirring. The material insoluble upon such treatment retained the protactinium nearly quantitatively. Considerable amounts of titanium were removed in the supernatant, but titanium remained the principal constituent of the insoluble material. Zirconium was also present in appreciable concentration, but niobium and tantalum, which might have been expected to concentrate along with the protactinium, were not detectable spectrographically.

In processing most of the material the residue from nitric acid-hydrogen peroxide treatment was leached repeatedly with a solution 5N in nitric acid and 0.3N in hydrofluoric acid. All the protactinium along with about half the total solids was removed in these leaches. The leaches were evaporated to dryness with perchloric acid, and the residue was again treated with nitric acid and hydrogen peroxide to remove titanium. The bulk reduction accomplished in this repetition of the hydrogen peroxide treatment was hardly sufficient to justify the time required. This is especially true in view of the

fact that titanium and zirconium, which constitute the great bulk of material remaining with the protactinium after the manganese dioxide cycles, are so efficiently removed by the use of anion-exchange resins and solvent-extraction procedures employed in the subsequent purification of the protactinium. Furthermore, the protactinium present in the residue following the second hydrogen peroxide treatment was not readily leached from the mixture by even concentrated hydrofluoric acid. This behavior considerably complicated the ensuing purification steps.

4. ISOLATION OF PROTACTINIUM

The chief impurities present with the protactinium, following the concentration procedure described above, are titanium and zirconium. It is perhaps improper to speak of them as impurities since they actually constitute 99.9 per cent or better of the material in hand. Two properties of protactinium were the principal factors in effecting its separation from this material. These were (1) its ability to form a stable complex anion with fluoride ion, which is readily absorbed in a column of amberlite IR-4 anion-exchange resin,⁹ and (2) its extractability into diisopropyl ketone from strong nitric¹⁰ or hydrochloric acid solutions.⁴

The residue from the second peroxide treatment was treated with about 20N hydrofluoric acid; this effected the solution of somewhat more than half the bulk material. About 50 per cent of the protactinium, however, remained with the insoluble residue. Qualitative tests showed the major constituent in the acid solution to be titanium, whereas the major constituent in the insoluble residue was zirconium (probably present as an insoluble fluozirconate). In the following discussion hydrofluoric acid solution will be referred to as the "titanium fraction" and the insoluble residue as the "zirconium fraction." It should be borne in mind that after the first hydrogen peroxide treatment the protactinium was completely soluble in hydrofluoric acid, and the necessity for working up a zirconium fraction would have been eliminated had a second peroxide treatment been avoided.

The zirconium fraction was brought into solution by metathesis with 2N sodium hydroxide followed by solution of the hydroxides in 1N nitric acid. The zirconium and protactinium hydroxides were reprecipitated once and washed with 0.1N alkali to remove the last traces of fluoride ion, which, if present, would have interfered with subsequent solvent-extraction operations.

A similar hydroxide precipitation procedure might have been employed to separate fluoride from the titanium fraction. Instead,

however, advantage was taken of the stability of the protactinium fluoride complex ion in order to effect a partial separation of the protactinium from titanium. The concentrated hydrofluoric acid solution of the titanium fraction, about 500 ml, was diluted to 2.5 liters with water, and the solution was passed through an anion-exchange adsorption column. The column (constructed of 100-ml lusteroid tubes with the bottoms removed, sealed end to end with Duco cement) was 30 cm in diameter, and the resin bed was 45 cm long. Twenty- to thirty-mesh amberlite IR-4 was used as the adsorbent. The solution was passed through the column at the rate of 1 liter/hr, and 99 per cent of the protactinium was adsorbed. The column was then rinsed with 700 ml of water and 500 ml of 0.1N nitric acid with no loss of protactinium. The protactinium was eluted with 1N nitric acid, 90 per cent of the protactinium present coming off with only a few per cent of the titanium. The remaining 10 per cent of the protactinium was eluted with about 50 per cent of the titanium. The protactinium (about 10 mg) was obtained in a volume of 1 liter of 1N nitric acid containing about 140 mg of titanium. The hydroxides of protactinium and titanium were precipitated and washed to remove the last traces of fluoride ion. Solution of this hydroxide precipitate in 100 ml of 3N nitric acid resulted in the formation of a colloidal titanium solution unsuitable for solvent extraction. Addition of hydrogen peroxide to a concentration of 0.3 per cent converted the titanium to the brilliant red titanium peroxide complex ion, and it was possible to extract the protactinium from this solution using diisopropyl ketone.

Conditions for the extraction of tracer concentrations of protactinium into diisopropyl ketone have been described in a previous paper.¹⁰ Conditions for the extraction of macro concentrations of protactinium from solutions containing relatively high concentrations of impurities were found to be somewhat more critical. Commonly employed salting agents such as manganese or calcium nitrates result in the formation of colloidal solutions from which the protactinium cannot be extracted. Best results were obtained by using only nitric acid as a salting agent. In the absence of peroxide and using equal volumes of aqueous and ketone phases, 65 per cent or more of the protactinium extracts into the ketone phase at acidities of 4N to 6N. From the 0.3 per cent peroxide solutions of the titanium fraction, adequate extraction was obtained only at acidities of 7N or higher. From 4.5N HNO_3 , the extraction was 3 per cent, and from 5N HNO_3 it was 14 per cent. From 6.7N HNO_3 , the extraction amounted to 65 per cent. It was also found necessary to

avoid heating dilute nitric acid solutions of impure protactinium since precipitates often formed which were not readily dissolved.

A set of five 250-ml centrifuge bottles was used for the solvent extraction. Bottle 1 contained the impure protactinium in nitric acid solution of sufficient strength to salt at least 65 per cent of the protactinium into an equal volume of ketone. Bottles 2 and 3 contained 75 ml of 0.3 per cent hydrogen peroxide in water. Bottles 4 and 5 contained 75 ml of 3.0 per cent peroxide in water. The solution in bottle 1 was equilibrated with successive portions of diisopropyl ketone. To prevent extraction of nitric acid from bottle 1, this ketone was preequilibrated with a water solution of the same acidity. The equilibration was accomplished by vigorous mechanical stirring for 2 to 3 min. Each portion of ketone after removal from bottle 1 was equilibrated successively against the solutions in bottles 2, 3, 4, and 5. Nitric acid and impurities are removed from the ketone by the aqueous layers of bottles 2 and 3. Then, with the acid concentration in the ketone reduced to a low value, equilibration against 3 per cent peroxide in bottle 4 results in an essentially quantitative removal of the protactinium from the ketone layer and in its precipitation as the white peroxide. When nitric acid has accumulated in bottle 4 to such an extent that an appreciable amount of protactinium is observed to be passing over into bottle 5, bottle 4 is removed and replaced in the system by bottle 5, which in turn is replaced by a fresh solution of 3 per cent hydrogen peroxide. Nitric acid accumulates in bottles 2 and 3, and these solutions are replaced by fresh solutions after equilibration with several portions of ketone.

The peroxide slurries from bottle 4 were approximately 1N in nitric acid. They occupied a combined volume of about 250 ml, and the solubility of the protactinium peroxide was about 1 mg per liter. The peroxide precipitate was separated by centrifugation, washed with a solution of 0.1N nitric acid and 3 per cent hydrogen peroxide, and dissolved in 50 ml of 8N nitric acid by heating for 45 min at 100°C. A spectrographic analysis on a portion of this slightly turbid solution showed the following impurities: Zr, 0.75 per cent; Si, 0.75 per cent; Ca, 0.25 per cent; and Mg, 0.05 per cent.

After standing for several days a solid phase separated from the 8N nitric acid solution. The solubility was about 0.3 mg of protactinium per milliliter. This precipitate was redissolved in additional acid, and the entire batch was repurified by another diisopropyl ketone extraction. The impurities mentioned above were completely eliminated by this treatment. A total of slightly more than 20 mg of pure protactinium was obtained by this procedure.

5. ANALYTICAL CONTROL AND PROCESS PERFORMANCE

Of the alpha activity present in the original carbonate residue, about 5 per cent was due to protactinium; most of the rest was attributable to ionium; and a few per cent to polonium. To follow the course of the protactinium in the early concentration stages would therefore have required separation of the protactinium from the ionium and polonium before measurement of alpha activity. Procedures for this separation have been described, but they are rather time consuming and were therefore not employed routinely. It was possible to determine the percentage of the alpha activity present in the third manganese dioxide precipitate which is attributable to protactinium, polonium, and ionium by measuring the energy distribution of the alpha particles in a pulse analyzer.¹¹ Such a determination was not possible earlier in the process because very thin samples must be prepared in order to avoid self-absorption. The results of such pulse analyses on the third manganese dioxide precipitate from the first four 10-kg batches are shown in Table 1.

The radiochemical assay values quoted in Table 1 were obtained using a simplified procedure which proved quite useful for the particular purpose. A small portion of the manganese dioxide precipitate was dissolved in 1 ml of 1N nitric acid containing 1 drop of 6 per cent hydrogen peroxide solution. One milligram of thorium is added as a drop of a thorium nitrate solution, and thorium fluoride is precipitated by making the solution 4N in hydrofluoric acid. After digestion for 5 min at room temperature the thorium fluoride is separated by centrifugation. The ionium present is practically quantitatively removed by this precipitation, while protactinium and polonium remain in the supernatant. An aliquot of the supernatant is evaporated on a platinum disk which is heated to redness in the flame of a Meker burner. Separate tests using pure polonium and pure protactinium tracers have shown that, when evaporated from fluoride solution and ignited in this manner, more than 95 per cent of the polonium and less than 2 per cent of the protactinium is volatilized.

Throughout the isolation procedures protactinium is the only alpha emitter present, and analytical control is therefore no problem.

The total performance of the process is indicated in Table 2, which lists the losses encountered through the concentration steps. No significant losses were encountered in the isolation steps since all waste solutions were easily reworked. It must be remembered in considering Table 2 that it includes data from several early runs in which very large losses were sustained. Thus the protactinium recovery from batches 5 and 6 were 16 and 14 per cent, respectively.

These very low yields were occasioned by large losses in the first manganese dioxide precipitation which was performed at too low a temperature and remained largely colloidal suspended. A more just appraisal of the behavior of the process is afforded by a consideration of the last six batches which were processed, in which an average of 65 per cent of the protactinium originally present was recovered through the concentration steps.

ACKNOWLEDGMENT

The authors wish to record their indebtedness to Leonard I. Katzin for his many valuable suggestions during the development of this process.

Table 1—Alpha Activities Present in Third MnO_2 Precipitate

Batch No.	Distribution of α activity according to pulse analysis			Protactinium present, mg	
	Io, %	Po, %	Pa, %	Pulse analysis	Radiochemical assay
1	60	6	34	0.50	0.57
2	49	5	46	0.68	0.70
3	20	40	40	0.95	0.92
4	2	35	63	0.71	0.83

Table 2—Protactinium Balance Sheet through Concentration Steps

	%	Mg
Losses		
In MnO_2 supernatant (by difference)	44.5	20.1
In insoluble residue from solution of 1st MnO_2 precipitate	4.6	2.1
In insoluble residue from solution of 2d and 3d MnO_2 precipitate	2.7	1.2
In HNO_3 - H_2O_2 supernatant	1.1	0.5
Total losses	52.9	23.8
Recovered through concentration steps	47.1	21.2
Pa content of 225-kg carbonate residue (0.2 ppm)	100	45.0

Fig. 1 — Process flow sheet for 10-kg batch.

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Paper 6.6

HALF LIFE OF Pa^{231}

By Q. Van Winkle, Raymond G. Larson, and Leonard I. Katzin

[Editor's note: This paper was a contribution from the Argonne National Laboratory and is based on Report ANL-4095.]

1. INTRODUCTION

The half life of protactinium (Pa^{231}), the parent of actinium in the actino-uranium decay series, has been determined by a number of investigators. Values have been reported which range from 12,500 to 32,000 years.¹⁻³ In view of the indirect methods used in the determinations and their wide scatter, a redetermination of the protactinium half-life value has been made through direct determination of the specific activity with the aid of modern methods for counting alpha particles. A value of $34,300 \pm 300$ years has been found, using the formula Pa_2O_5 for the ignited oxide of protactinium.

2. EXPERIMENTAL WORK

Two samples of protactinium oxide were used in the half-life determinations. The first was taken from material which had been isolated and purified by Larson, Katzin, and Hausman;⁴ the second was taken from a preparation which had been isolated and purified by Thompson, Van Winkle, and Malm.⁵ These samples were given an additional purification by precipitating protactinium as the hydrated oxide from 0.5N to 1N nitric acid either by heating on a boiling-water bath for 5 min (sample 1) or through precipitation with hydrogen peroxide added to 3 per cent concentration (sample 2).

Samples of hydrated oxide were slurried into platinum crucibles using 1N nitric acid and then dried and ignited to constant weight in a muffle furnace at 700 to 800°C. Weighings were made on a semi-

micro balance with a sensitivity of 0.15 scale divisions per 10 μg . After ignition to constant weight the oxide was made soluble by adding concentrated hydrofluoric acid and evaporating to dryness. The dried material was dissolved in 6N hydrochloric acid solution (sample 1) or 1N nitric acid (sample 2) and made up to volume. Aliquots of these two solutions were evaporated on platinum counting disks for determination of the alpha-emission rate. Results are based on four aliquots of sample 1 and six aliquots of sample 2.

Aliquots from both sample solutions were analyzed spectrographically for impurities in the protactinium.

Determinations of alpha-particle emission rate were made with a counter having a mixture of argon and carbon dioxide at atmospheric pressure flowing through the chamber. The counter has been described by Jaffey.⁶ Its effective counting yield is 51.7 per cent, and its coincidence loss has been estimated as 1.26 per cent per 100,000 c/min.

3. RESULTS

The data obtained have been summarized in Table 1. The values appearing in line 2 for the weight of oxide were obtained by correcting the weight in line 1 for the impurities revealed by the spectrographic analysis. The corrections were made on the basis of the corresponding oxides. Sample 1 contained 1.5 per cent iron, 0.15 per cent calcium, and 0.035 per cent magnesium by weight. Impurities in sample 2 were less than the minimum detectable amounts, so no correction was made. Assuming a formula for the oxide of Pa_2O_5 , the half life of the protactinium is calculated, using the relation $\lambda T = \ln 2$, where λ is the disintegration constant and T is the half life. Since the two samples give the same half-life value within experimental error, the rather more precise value of sample 2 is taken, namely, $34,300 \pm 300$ years.

The largest uncertainty in the measurements may actually be the structure of the ignited protactinium oxide. We are indebted to W. H. Zachariasen for a study of the x-ray structure of the powder. Although the patterns obtained are complex, there seems to be evidence for a possible PaO_2 structure. If the composition of the ignited material is actually the dioxide composition, the half-life value given would be low by approximately 3 per cent.

4. DISCUSSION

The value reported in this study for the Pa^{231} half life, 34,300 years, is higher than any appearing in the literature. The closest cor-

response is found with the 1932 value of Von Grosse, namely, 32,000 years.³ This value was obtained from presumed pure macro amounts of the isotope; the values given in the earlier literature are based on growth into purified uranium of the protactinium. These early determinations depend on measuring current intensities in an alpha electroscope, knowing the number of ion pairs produced for both protactinium alphas and U^{238} alphas, and knowing precisely the ratio of activity of U^{235} and U^{238} in natural uranium. The method is beset with corrections and imperfectly known constants, and it is inherently inaccurate. Correction of the original data with more recently established values for the constants involved fails to raise the values to the level reported here, although a certain amount of consistency between different determinations by similar techniques can be found. The determination of Von Grosse with macro amounts of the isotope eliminated some sources of error, but the determination again was dependent on knowledge of the number of ion pairs produced per alpha particle and comparison with alpha emission of uranium as measured in an electroscope. A source of error unknown to Von Grosse is the fact that one-eighth the alpha particles emitted by protactinium differ in energy from the rest by some 300 Kev.^{7,8} The determination by direct counting of alpha particles, as carried out in the experiments reported here, is therefore the least questionable of the procedures used. The uncertainty of the experimental value is probably well below 1 per cent. A revision of approximately 3 per cent must be made in the value if it is shown that the protactinium oxide obtained under the experimental conditions described in this paper is PaO_2 rather than the expected Pa_2O_5 .

ACKNOWLEDGMENT

We wish to thank Frank Tomkins for performing the analyses of the sample solutions.

Table 1 — Half-life Data of Pa^{231}

	Sample 1	Sample 2
Weight of ignited oxide, mg	0.72	2.86
Corrected weight of oxide, mg	0.705	2.86
Solution volume, ml	5.00	49.63
Aliquot (λ)	25.0	50.35
Average counting rate (corrected) of aliquot (51.7% counting yield)	153,500	128,100
Specific activity, c/min/g of Pa	5.11×10^{10}	5.18×10^{10}
Half life, years	34,700	34,300

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Paper 6.7

SOLUBILITY OF PROTACTINIUM IN COMMON ACIDS

By Roy C. Thompson

[Editor's Note: This paper was a contribution from the Argonne National Laboratory and is based on Report CC-3637.]

ABSTRACT

A preliminary study of the solubility of protactinium in nitric, hydrochloric, sulfuric, perchloric, and hydrofluoric acids leads to the conclusion that such solubility as is exhibited in acid solution may be attributed largely, if not entirely, to the formation of complex ions.

1. INTRODUCTION

A preliminary study has been made of the solubility of protactinium in nitric, hydrochloric, sulfuric, perchloric, and hydrofluoric acids. The purpose of this study was only that of supplying the preliminary data necessary before an extensive program on the solution chemistry of protactinium could be undertaken. In no case was the solid phase studied, and the period of equilibration was in some instances too short to allow the attainment of final equilibrium. The results should nevertheless be of considerable practical interest.

2. EXPERIMENTAL WORK

The protactinium employed had been isolated from uranium extraction residues.¹ Spectrographic analyses were not performed on all the samples employed; however, all the material had been purified exhaustively by diisopropyl ketone extraction which has been demonstrated to yield spectrographically pure material.¹ The reagents employed were not specially purified but were of the best grade commercially available.

Equilibrations were performed in small glass tubes such as pictured in Fig. 1. The volume of each tube below the constriction was of the order of 0.1 ml. About 0.5 mg of protactinium was employed in each run, and the liquid volume was of the order of 0.05 ml. Continuous agitation of the solid phase was achieved by mounting the tubes horizontally on the perimeter of a wheel rotated slowly by an electric motor. A strip of "parafilm" was wrapped around the tube and ground-glass cover to ensure a tight seal. No attempt was made to regulate the temperature of the tubes during equilibration. However, the room temperature during the course of the experiments was not observed to vary by more than 1.5°C from 24.5°C. The tubes were centrifuged in an air-driven microcentrifuge. The tube covers were removed during this operation, and the open end was sealed with parafilm to prevent evaporation. The protactinium concentration in the supernatant was determined by evaporating an aliquot on a platinum plate and counting alpha disintegrations. All calculations were based on a half life of 34,400 years.² Except as otherwise indicated, samples were taken at intervals until a constant value for the solubility was obtained. Acidities were determined by microtitration of a sample (usually 0.010 ml) removed at the conclusion of each run. [Titrations were performed by Ralph Bane of the analytical group.]

Each run was set up initially in one of three manners:

1. A suspension of protactinium hydroxide in water was introduced into the tube, the water was evaporated, and the residue was dried for 1 hr or more under an infrared heat lamp. Acid of the approximate desired normality was then added.
2. A previous run using the same acid was diluted to the approximate desired normality.
3. A previous run was evaporated to dryness, and the residue was washed with water and dried for 1 hr or more under an infrared heat lamp. Acid of the approximate desired normality was then added.

3. RESULTS AND DISCUSSION

The results of these investigations are given in Table 1. In only one instance (run 3) was an obviously colloidal solution encountered. The very low solubility in even concentrated perchloric acid, together with the increasingly greater solubility in acids of increasing complexing ability, suggests strongly that whatever solubility is exhibited by protactinium in acid solutions may be attributed to the formation of complex ions. It is interesting to note that in the case of both nitric and sulfuric acids a maximum solubility is attained at an intermediate acidity. This is especially noticeable in the case of sulfuric acid. Only one run was made with HF, and the results can be considered of only

qualitative significance since the experiment was conducted in glass.

It should be noted that often, when attempting to dissolve completely protactinium in strong nitric acid, much lower apparent solubilities have been observed than those indicated in Table 1. In these cases, however, most of the protactinium dissolves in a small amount of acid, as would be predicted from the values in Table 1, and the addition of more acid results in very little additional solution of protactinium. This suggests that a small portion of the protactinium may exist in a state which has a much lower solubility. Since a relatively large excess of the solid phase was present in all the solubility tests reported in this paper, it is probable that the more soluble state was always present in excess, and consequently the results obtained are applicable only to this more soluble state, not necessarily to protactinium in general.

Table 1—Solubility of Pa in Common Acids

Run No.	Acid	N	Solubility, g/liter	Time of equilibration, days	Starting material	Remarks
1	HClO ₄	11.1	0.030	4	Hydroxide	
2	HClO ₄	7.10	0.0027	5	Dilution	
3	HClO ₄	1.73	(0.044)	7	Dilution	Colloidal solution M.W. $\sim 1-20 \times 10^6$
4	HCl	9.61	0.30	24	Hydroxide	Solution after 4-hr equilibration = 1.2 mg/ml
5	HCl	4.90	0.010	5	Dilution	
6	HCl	3.33	0.0085	13	Dilution	
7	HCl	0.99	0.0015	6	Dilution	
8	HNO ₃	15.3	4.2	4	Hydroxide	
9	HNO ₃	13.8	6.6	13	Evaporation of HNO ₃	
10	HNO ₃	9.44	5.5	3	Dilution	
11	HNO ₃	5.66	0.043	6	Dilution	Solution after 2-day equilibration = 0.20 mg/ml
12	HNO ₃	1.88	0.0056	13	Hydroxide	
13	HNO ₃	1.17	0.0037	6	Hydroxide	
14	H ₂ SO ₄	32.5	0.093	16	Evaporation of H ₂ SO ₄	
15	H ₂ SO ₄	21.9	1.8	3	Dilution	
16	H ₂ SO ₄	17.9	0.91	24	Hydroxide	Solution after 5-hr equilibration = 5.10 mg/ml
17	H ₂ SO ₄	9.93	3.3	9	Dilution	
18	H ₂ SO ₄	8.89	6.8	1	Dilution	
19	H ₂ SO ₄	8.78	(1.4+)*	3	Evaporation of HNO ₃	Solution after 1-day equilibration = 0.57 mg/ml
20	H ₂ SO ₄	5.66	(5.7+)*	7	Hydroxide	Solution after 1-day equilibration = 0.80 mg/ml
21	H ₂ SO ₄	0.92	0.78	3	Dilution	
22	HF	0.05	3.9	1 hr	1N HNO ₃	In glass, solution at 4 days = 0.93 mg/ml

*These runs had not attained equilibrium when discontinued.

Fig. 1 — Sample of small glass tubes used in equilibrations.

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Paper 6.11

CHEMISTRY OF PROTACTINIUM. I. SOME OBSERVATIONS
ON SOLVENT EXTRACTION OF PROTACTINIUM

By Kurt A. Kraus and Q. Van Winkle

[Editor's Note: This paper was a contribution from the Metallurgical Laboratory and is based on Report ORNL-239.]

ABSTRACT

Protactinium was found to be extractable from hydrochloric acid solutions by organic solvents (diisopropyl ketone). Addition of peroxide or oxalate decreases the extractability. However, even in the presence of these complexing agents, good extraction can be obtained if the acid concentration is sufficiently high.

1. INTRODUCTION

During an investigation of isolation procedures of milligram amounts of protactinium (Pa^{231}), a number of collateral observations have been made on the chemical properties of this element in various aqueous and nonaqueous media. Since this work has not been continued, it appears desirable to publish the results at this time, although many of the observations can only be considered to be of preliminary nature.

2. SOLVENT EXTRACTION OF PROTACTINIUM FROM
HYDROCHLORIC ACID SOLUTIONS

Hyde and Wolf¹ found that protactinium could be readily extracted by diisopropyl ketone in the presence of nitric acid, provided the nitric acid concentration was larger than about 1M. These experiments had been carried out on a tracer scale. Experiments at macro

concentrations (of the order of milligrams and grams of Pa^{231} per liter), however, showed² that often protactinium cannot be extracted readily from nitric acid solution and that it tends to hydrolyze and precipitate from these solutions. Since the solubility of protactinium in nitric acid solution is apparently very low and since the precipitate which results in such solutions is quite refractory, solvent extraction from nitric acid does not appear to be feasible at high Pa concentrations.

The extractability of protactinium from hydrochloric acid solutions was of interest, and a tracer-scale investigation indicated that protactinium can be readily extracted. The experiments were carried out with Pa^{233} tracer [beta emitter, half life ($T_{1/2}$) = 27.4 days] on a 50- μl scale using equal volumes of aqueous and organic phases. Typical results are summarized in Table 1. It can be seen that in hydrochloric acid solutions as low as about 2M the solubility of protactinium in the solvent is sufficiently high for most purifications with distribution coefficients D (concentration of Pa in organic phase divided by its concentration in the aqueous phase) larger than unity.

As mentioned above, in the extraction of Pa from HNO_3 solutions, difficulties are encountered when macro concentrations of Pa are involved. These difficulties are probably due to hydrolytic polymerization of the Pa, which makes the Pa inextractable. Complexing of Pa by nitrate even in practically concentrated HNO_3 appeared not to be sufficiently strong to prevent this.

It is of interest that similar difficulties were not found with HCl solutions of Pa where the distribution coefficients for tracer solutions and for solutions of macro concentrations were approximately the same. Thus it appears that Pa is considerably more strongly complexed by chloride ions than by nitrate ions and that chloride ions more effectively inhibit its hydrolysis and hydrolytic polymerization.

The high extractability of Pa from HCl and HNO_3 solutions (at low Pa concentration in the latter case) suggests strongly that Pa can be present in an ionically dispersed form under some conditions since it is not expected that a polymeric form of Pa would readily extract. This conclusion also is based on the observation that extraction of Pa becomes difficult under conditions where polymerization is likely² and that extraction of Pu(IV) by organic solvents is also inhibited by polymerization.³

3. EXTRACTION OF PROTACTINIUM FROM PEROXIDE SOLUTIONS

Addition of hydrogen peroxide to protactinium solutions was found to decrease its extractability by diisopropyl ketone. Typical results

illustrating this effect are shown in Table 2 and Fig. 1. In these experiments 5M HCl solutions of Pa^{233} were equilibrated with equal volumes of solvent on a micro scale. The extractability was determined as a function of time, and the data were extrapolated back to zero time to correct for the decomposition of the hydrogen peroxide. The changes in extractability on addition of hydrogen peroxide are similar to those expected from the fact that protactinium forms an insoluble peroxide if its concentration is sufficiently high. Since the decrease in extractability is, however, only moderate, it appears possible that a soluble peroxide complex of Pa exists which is extractable. This conclusion is also supported by the observations that Pa can be extracted from a slurry of its peroxide.

The extractability of protactinium from peroxide solutions is highly dependent on HCl concentration, as is shown in Table 3 and Fig. 2, where the extractability of Pa^{233} tracer is shown as a function of HCl concentration at constant peroxide concentration (3 per cent H_2O_2). The experiments reported in Table 3 were carried out using the same technique as was used for the experiments in Table 2.

4. EXTRACTION OF PROTACTINIUM FROM OXALATE SOLUTIONS

Since the extractability of protactinium by diisopropyl ketone is very high even at acidities as low as 1M HNO_3 , reextraction of Pa by water from the organic layer often becomes difficult. The organic layer usually extracts large amounts of acid from the aqueous layer so that on reextraction with an aqueous layer of low acidity sufficient acid is reextracted into the aqueous phase to make the distribution coefficient quite unfavorable. It was shown in a previous paper² that addition of oxalate to the aqueous layer decreases the distribution coefficient sufficiently that reextraction of Pa by water is feasible with 1M HNO_3 . The distribution coefficients in oxalate solutions, however, are highly acid dependent, as is shown in Table 4 and Fig. 3. Therefore at HNO_3 concentrations larger than about 2M more than 25 per cent of the Pa can be extracted in one equilibration with an equal volume of ketone.

To prepare the aqueous oxalic acid-Pa solutions for reextractions by the solvent, it was suggested² that the oxalic acid be oxidized with a suitable oxidizing agent, e.g., Ce(IV). The observed rapid increase of the distribution coefficients of Pa with acidity in the presence of oxalate, however, indicates that this procedure was unduly cumbersome. It appears to be sufficient for solvent extraction of the oxalate solutions to increase the acidity of the aqueous layers, e.g., to about 5M.

In similar experiments, carried out somewhat later, considerably higher extractabilities were observed (Table 5). The reason for the discrepancy is not definitely known since the experiments at either time were quite reproducible. [Note: It is possible that different solvents were used in the two series of experiments (Tables 4 and 5) since it is believed that at one time a batch of diisopropyl ketone was used which was actually a mislabeled batch of diisopropyl carbinol. As a matter of fact, all the experiments described with diisopropyl ketone in this and a previous² paper may have been carried out with the carbinol. Since this material is not now available for recheck and analysis, this point cannot be resolved. However, more recent experiments with diisopropyl carbinol³ showed consistently higher distribution coefficients for HCl solutions than those given in Sec. 2, this paper, making it probable that the bulk of the experiments in this paper were actually performed with the ketone and that only those given in Tables 5 and 6 were performed with the carbinol.] Similarly, a test of the extractability as a function of time indicated that essential equilibrium was established after a few minutes' shaking (Table 6).

Table 1—Extraction of Pa²³³ from HCl Solutions

Molarity of HCl	0.8	2.4	4.8	7.2	9.6
Pa in ketone, %	10	55	72	71	73
D	0.11	1.2	2.6	2.5	2.7

Table 2—Change of Extractability of Pa²³³ in 5M HCl with Peroxide Concentration

H ₂ O ₂ , %	0	1.0	3.0	5.0
Pa in ketone, %	72	45	24	16
D	2.6	0.82	0.32	0.19

Table 3—Extraction of Pa²³³ from HCl-3 Per Cent H₂O₂ Solutions

Molarity of HCl	1.0	3.0	4.0	5.0	7.0
Pa in ketone, %	0.5	1.0	7.0	24	45
D	0.005	0.010	0.075	0.32	0.82

Table 4—Extraction of Pa²³³ from 0.1M Oxalic Acid Solutions

Molarity of HNO ₃	1.0	2.0	3.0	4.0	6.0	8.0
Pa in ketone, %	0.3	24	43	52	69	71
D	0.003	0.32	0.75	1.1	2.2	2.4

Table 5—Extraction of Pa²³³ from 0.1M Oxalic Acid Solutions*

Molarity of HNO ₃	2.0	4.0	6.0	8.0
Pa in ketone, %	4.0	60.66	88.90	89.90
D	0.042	1.7	8.1	8.5

*See Note, Sec. 4, this paper.

Table 6—Extraction of Pa²³³ from 0.1M Oxalic Acid Solutions
as Function of Time*

	Time, min					
	5	20	60	120	210	Average
2.6M HNO ₃	17.1	17.8	18	16.6		17.4
5.3M HNO ₃	85	90	86		85	87

*See Note, Sec. 4, this paper.

Fig. 1—Extractability of Pa^{233} from $\text{HCl-H}_2\text{O}_2$ mixtures (diisopropyl ketone).

Fig. 2 — Extractability of Pa^{233} from $\text{HCl-H}_2\text{O}_2$ mixtures (5M HCl).

Fig. 3 — Extractability of Pa^{233} from HNO_3 - $\text{H}_2\text{C}_2\text{O}_4$ mixtures (0.1M $\text{H}_2\text{C}_2\text{O}_4$).

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Paper 6.12

CHEMISTRY OF PROTACTINIUM. II. A METHOD OF ANALYSIS OF ORE RESIDUES FOR PROTACTINIUM

By Kurt A. Kraus and Allan Garen

[Editor's Note: This paper was a contribution from the Oak Ridge National Laboratory and is based on Report ORNL-300. The assistance of F. L. Moore in the initial stages of the work is gratefully acknowledged. A brief description of the method has previously been given in Report CL-KAK-26, May 1947.]

ABSTRACT

A rapid method for the analysis of ore residues for Pa^{231} is described. The method involves HF leach of the residue, zirconium iodate precipitation, solvent extraction, and differential α -range analysis.

1. INTRODUCTION

Using some of the steps of the isolation procedure for Pa^{231} [alpha emitter, $T_{1/2} = 34,400$ years (Von Grosse gave $T_{1/2} =$ about 32,000 years)]^{1,2} from ore residues, which was previously described,³ a rapid analytical procedure for Pa^{231} was developed. Although the general applicability of the method has not been tested, it appears that it should be useful for the analysis for Pa^{231} in general, without major modifications.

2. DESCRIPTION OF METHOD

The analytical procedure essentially consists of three parts:

1. Leaching of the protactinium from the ore residues.
2. Concentration of protactinium and removal of sufficient extraneous material to prepare a "thin" counting plate, using added Pa^{233} tracer to estimate chemical yield.

3. Alpha-range analysis to determine the proportion of protactinium alphas to total alphas in the final sample.

The amount of residue needed for analysis is determined by the amount of activity needed for satisfactory range analysis, which amounted to about 2000 dis/min for the analyzer used in this work.

[Note: We are indebted to J. H. Parsons for all range analyses.]

The weighed samples were placed in a platinum dish, moistened with a minimum amount of water, and treated with about 3M HNO_3 until gas evolution (due to carbonates in the residues) stopped. To the suspensions, sufficient Pa^{233} (β emitter, $T_{1/2} = 27.4$ days)⁵ was added as tracer to "drown out" the natural beta activity of the sample. In this way beta assay could be used to estimate the protactinium yields. Concentrated hydrofluoric acid and a drop of concentrated sulfuric acid were added to the mixture, and the suspension was heated under an infrared lamp for about $\frac{1}{2}$ hr to leach out the bulk of Pa^{231} from the ore residue and at the same time to provide a medium in which exchange between Pa^{231} and the added Pa^{233} tracer should occur. After cooling, the suspension was centrifuged, and the residue was washed with hydrofluoric acid and then discarded. To remove hydrofluoric and fluosilicic acids, the supernatant and washings were heated under a heat lamp until strong fumes of SO_3 came off. During the heating some material separated from the solution. However, most of it could be dissolved with a small amount of 5M HNO_3 in about $\frac{1}{2}$ hr at room temperature. After this time the mixture was centrifuged, and the residue was discarded. The supernatant usually contained more than 75 per cent of the protactinium of the HF extract, as indicated by beta assay. The effectiveness of the hot hydrofluoric acid treatment for extraction of Pa^{231} from the ore residues had previously been established³ and was rechecked several times.

Concentration of the Pa from these extracts was achieved by carrying it on zirconium iodate, using about 0.1 mg of Zr per milliliter of solution. The zirconium iodate was dissolved in a minimum quantity of concentrated HCl. A silver strip was inserted to remove polonium (Po^{210} , α emitter, $T_{1/2} = 140$ days).⁵ Contact of the solution with the silver strip for 1 hr was usually sufficient, although at times overnight contact appeared necessary.

Further purification, particularly from zirconium, was achieved by solvent extraction of the hydrochloric acid solution using diisopropyl carbinol. In general, more than 80 per cent of the protactinium was extracted with one equilibration of solvent (using equal volumes of aqueous and nonaqueous phase) if the hydrochloric acid solutions were 2M to 4M. The carbinol was evaporated directly onto a platinum plate for alpha and beta analysis as well as for range

measurements. The total beta count of the sample was used to estimate chemical yield throughout the analysis, and the concentration of Pa^{231} was obtained from combination of total alpha count of the sample and range analysis. The latter gives the ratio of protactinium alphas to total alphas. In general, it was found that more than 90 per cent of the alpha activity of the "final" plates was due to Pa^{231} .

The bulk of the α activity of the ore residues was due to polonium and ionium (Th^{230} , $T_{1/2} = 83,000$ years).⁵ For satisfactory Pa^{231} range measurement they should be removed as completely as possible if an instrument of rather limited resolution power is used, since the α energies of the three isotopes are not very different:⁵

Io^{230}	about 4.7 Mev
Po^{210}	5.30 Mev
Pa^{231}	about 5.00 Mev (85 per cent)
Pa^{231}	about 4.72 Mev (15 per cent)

As mentioned earlier, Po was removed from an HCl solution by permitting it to deposit on a silver strip. The other steps in the analysis, including the solvent-extraction step,³ do not cause separation from Po. The ionium was probably held back in the original hydrofluoric acid treatment of the ore residue, at which time it would be expected to be carried by the insoluble fluorides. However, the solvent-extraction step also would cause effective purification from ionium.

For satisfactory range analysis two requirements should be met:

1. The material on the final counting plate must be essentially weightless to permit high resolution of the α energies.
2. A considerable fraction of the alpha activity of the final sample should be due to Pa^{231} to give sufficient precision.

The rather simple analytical procedure described yielded final samples which were very satisfactory from both points of view. As mentioned earlier, more than 90 per cent of the alpha activity was due to Pa^{231} ; and, in general, the plates did not contain any visible amount of extraneous solid materials.

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Paper 7.1

DISSOLUTION OF THORIUM METAL AND THORIUM DIOXIDE IN HNO_3 -HF AND HNO_3 -(NH_4) $_2$ SiF $_6$ MIXTURES

By Frederick W. Schuler, Frank L. Steahly, and Raymond W. Stoughton

[Editor's Note: This paper was a contribution from the Clinton Laboratories and is based on Report CC-3576.]

ABSTRACT

A satisfactory method has been found for dissolving thorium metal and thorium oxide in heat-treated 25-12 stainless steel vessels without excessive corrosion of the vessels. The dissolution medium consists of strong HNO_3 containing a small amount of fluoride or fluosilicate. The fluoride required has no harmful effects on a subsequent solvent-extraction step for a separation of uranium isotopes from the dissolved thorium.

1. DISSOLUTION OF Th AND ThO_2 IN HNO_3 CONTAINING FLUORIDE OR FLUOSILICATE

In view of the interest in thorium in connection with piles for production of U^{233} (resulting from neutron capture followed by two successive beta emissions), it was desirable to find a convenient method for dissolving metallic thorium and the dioxide, since the anticipated methods of separation of the U^{233} from thorium involved starting with an aqueous solution of thorium nitrate. Because of the desirability, from an engineering standpoint, of using stainless steel vessels, it was hoped that a medium for the dissolution of the metal could be found which would not excessively corrode stainless steel. Although the basic carbonate, which is soluble in nitric acid, had been used in small-scale irradiations, it was not considered satisfactory for large-scale bombardments because its heat conductivity would not permit

sufficiently rapid removal of the tremendous amounts of energy given off by the initial (n, γ) reaction, the two successive beta emissions, and the small amount of U^{233} fission. Satisfactory substances seemed to be the metal itself and a slurry of the dioxide.

According to the literature, the metal was said to be readily soluble in aqua regia, more slowly so in hydrochloric acid, and rendered passive by pure nitric acid. The dioxide was said to be insoluble in HCl or HNO_3 and converted to the sulfate by hot concentrated H_2SO_4 . The sulfate is only moderately soluble in water.

Since solvent extraction appears to be the most attractive method for separating the U^{233} from the thorium after irradiation of the latter and since the contemplated process involved the extraction of the U^{233} from an aqueous thorium nitrate solution, it was desired that the thorium be converted to the nitrate in the dissolution step or to a compound which could in turn be readily converted to the nitrate. With this goal in mind the experiments now to be described were carried out during the fall of 1944. Nitric acid containing small amounts of fluoride as HF and H_2SiF_6 was tried as the first likely possibility. It was hoped that with low fluoride concentration the dissolution properties of the solvent would be satisfactory without the danger of excessive corrosion of the vessel or of the precipitation of thorium fluoride.

1.1 Dissolution of the Metal. A 90-g slab of thorium metal, cut from a larger piece made at Iowa State College under the direction of F. H. Spedding, was obtained for dissolution-test experiments. This slab of metal was cut into a number of small slices with which the dissolution tests were carried out. The results of these tests are given in Table 1.

From a comparison of the rates of solution in Expts. 3 to 7 it is seen that the dissolution rate is approximately proportional to the HF concentration at constant concentration of HNO_3 and at constant weight of metal. That the HF acts as a catalyst, rather than, for example, forms a permanent complex with the dissolved thorium, is seen from Expts. 6 and 7, where the final molar ratio of fluoride ion to thorium ion is about 0.03.

A rough qualitative picture of the effect of the ratio of metal surface to weight can be seen by comparing Expts. 10 and 6 and also 5 and 9. From Expts. 5, 8, and 11 it is seen that HNO_3 containing a small amount of HF or H_2SiF_6 [in this case the fluosilicate was added as $(NH_4)_2SiF_6$] will dissolve thorium metal as rapidly as pure HNO_3 dissolves uranium metal.

1.2 Dissolution of ThO_2 . A very pure grade of finely divided ThO_2 (i.e., particles of the order of 50μ in diameter) was obtained from

the Lindsay Light & Chemical Co. of West Chicago for the dissolution experiments with the dioxide. Each experiment involved having 0.5 g of ThO_2 and 10 ml of HNO_3 in the reaction vessel, heating the solution to 97°C where HF was used and to about 80°C where $(\text{NH}_4)_2\text{SiF}_6$ was used, and then adding the fluorine-containing reagent and heating at 100°C until all the oxide had dissolved. The recorded time is the time between the addition of HF or $(\text{NH}_4)_2\text{SiF}_6$ and the complete solution of the oxide. The results of these tests are given in Tables 2 and 3.

According to the results of Table 2, at constant but low concentrations of HF, thorium dioxide is appreciably more readily dissolved in 16N HNO_3 than in 8N HNO_3 . To be sure that this ThO_2 was not readily soluble in pure HNO_3 (in order to test the method of dissolution on a somewhat larger scale), three 10-g samples of ThO_2 were treated with 28 ml of 16N HNO_3 (i.e., three times the stoichiometric amount required to convert ThO_2 to the nitrate) as indicated in Table 4, with the results shown there.

The higher temperature is believed to be chiefly responsible for the shorter dissolution time required for sample a as compared to that for sample b, although the difference in pyrex and stainless steel vessels may also have been a contributing factor.

A 0.5-g sample of ThO_2 was heated in an evaporating dish in a Meker-burner flame until the evaporating dish had been held at red heat for several minutes. After this treatment 5 ml of an 8N HNO_3 -0.01N HF mixture failed to dissolve the sample in 30 min at 100°C , showing that this heat treatment caused the ThO_2 to be more difficult to dissolve. The HF concentration was raised to 0.02N, after which the sample dissolved during 30 min additional heating at 100°C . A similarly heated 10-g sample of ThO_2 did not dissolve in 22 ml of an 8N HNO_3 -0.01N HF mixture (this quantity of HNO_3 should result in a 1N HNO_3 solution after complete solution of the oxide) in 1 hr at 100°C or in 30 min additional treatment at this temperature after the HF concentration was raised to 0.02N. At this point 5 ml of concentrated HNO_3 was added, and the vessel was kept at 100°C overnight, resulting in complete solution of the oxide.

To test the effect of lowering the temperature on the dissolution of ThO_2 in HNO_3 -(NH_4) $_2\text{SiF}_6$ mixtures, each of three 0.5-g samples of our stock ThO_3 was treated with 5 ml of the acid mixtures at different temperatures: 100, 76, and 50°C . The results are presented in Table 5.

The results of Table 5 showed that, if it were necessary for reasons such as excessive corrosion, the dissolution of thorium dioxide could be carried out at a feasible rate at temperatures as low as around 75°C .

1.3 Larger Scale Dissolution of the Metal. The conditions chosen for dissolving thorium metal involved heating concentrated nitric acid containing 0.05M HF near the boiling point (see Sec. 2 for corrosion results). Several larger scale dissolution experiments have been conducted in the Oak Ridge National Laboratory Technical Division by F. L. Steahly, J. O. Blomeke, D. C. Overholt, and R. N. Leuze.¹ They found that thorium metal wafers 1.1 in. in diameter and $\frac{1}{2}$ in. thick (85 to 90 g each) were essentially completely dissolved in a 5 per cent excess of 40 to 60 per cent HNO_3 containing 0.05M HF in 23 to 30 hr. Actually a small amount of black thorium oxide remained undissolved, but this oxide should not be present in future metal production at Iowa State College, according to F. H. Spedding. With a 15 per cent excess acid 16 hr was required.

Since the rate of dissolution decreases as both the HNO_3 concentration and the metal surface area decrease and since it is desirable to finish with a low concentration of HNO_3 (rather than having to neutralize), it was considered more expedient to keep an excess of metal in the dissolver and to digest to a rather low concentration of free acid.

A sufficient quantity of a solution made up of 60 per cent HNO_3 and 0.05M HF was added to dissolve 86 g of a 175-g piece of metal, and the mixture was heated to boiling. It was found that 47, 74, and 86 g of metal had dissolved after $\frac{1}{2}$, $1\frac{1}{2}$, and $3\frac{1}{2}$ hr digestion, respectively, showing a considerable decrease in required time with excess metal present. It was found that some of the HNO_3 goes to NO_2 as well as to NO ; thus the metal dissolved per mole of HNO_3 consumed must be empirically determined.

2. CORROSION OF STAINLESS STEEL BY HNO_3 -HF AND HNO_3 -(NH_4)₂SiF₆ MIXTURES AT HIGH TEMPERATURES

After finding a suitable medium for dissolving thorium metal and thorium dioxide, it was necessary to determine the corrosion rate of this medium on materials from which dissolver vessels could be made. It was expected that heat-treated 25-12 stainless steel would be the best of the more common structural materials, with substances like niobium, tantalum, and platinum more resistant to corrosion though perhaps prohibitively costly for large-scale work.

A number of small-scale corrosion tests were carried out in the Technical Division at Oak Ridge National Laboratory under the general supervision of M. D. Peterson.²⁻⁴ Some of the results of these experiments are given in Table 6.

The figures given in Tables 6 and 7 are the maximum values obtained for each set of conditions and were obtained from weight losses

of the samples over 21- to 72-hr test periods. There was no evidence that pitting would be an important factor.

These results show that, at constant fluoride concentration, the corrosion rate decreases when thorium ion is present and as the HNO_3 concentration is decreased; and they suggest that under actual dissolving conditions a lower corrosion rate may be obtained than those indicated by Table 6. In order to show that this was actually the case, the results in Table 7 were then obtained by Peterson and Burris.⁵ Further corrosion studies by these two authors showed that the solutions resulting from the dissolution of thorium metal [in this particular case 2.5M $\text{Th}(\text{NO}_3)_4$, 1.0M HNO_3 , 0.05M HF] showed very little corrosion at 40°C on 18-8 stainless steel that had been heat-treated and on 18-8 and 25-12 stainless steel that had not been heat-treated. The actual figures obtained showed 0.00001 to 0.00002 in. per month for the first 64 hr of contact and considerably less for successive exposures of the same steel samples. Hence stainless steel that has not been heat-treated may be used for equipment other than the dissolver.

3. EFFECT OF FLUORIDE ION ON THE SEPARATION OF URANIUM FROM THORIUM BY SOLVENT EXTRACTION

While it was not supposed that small amounts of fluoride ion in an aqueous solution of high nitrate concentration would noticeably affect either the extraction of uranyl ion into organic solvents or the efficiency of its separation from large amounts of thorium by solvent extraction, it was nevertheless necessary to verify this supposition. The presence of 0.01N HF in an aqueous phase 1M in $\text{Al}(\text{NO}_3)_3$, 1M in HNO_3 , and 0.25M in $\text{Th}(\text{NO}_3)_4$ and containing U^{232} tracer was found to have no effect on the uranium-thorium separation. It was desirable to determine at what concentration of fluoride the separation would be affected and whether the separation could be improved by the holding of the thorium in the aqueous phase at, for example, a fluoride-to-thorium ratio of unity [see Sec. 4 for complexing of $\text{Th}(\text{IV})$ by fluoride].

Batch-extraction experiments were carried out on a 3-ml (in each phase) scale in which only the HF concentration was varied. The aqueous phases consisted of 0.87M $\text{Th}(\text{NO}_3)_4$, 0.83M $\text{Al}(\text{NO}_3)_3$, and 1M HNO_3 ; i.e., 7M total NO_3^- with enough U^{233} to act as uranium tracer, enough Th^{234} to act as thorium tracer, and enough HF present to give $\text{HF}/\text{Th}(\text{IV})$ ratios of 0, 1, or 2. The high nitrate concentration was chosen in order to make work possible under conditions where a significant fraction of both the thorium and uranium was extracted. These experiments were carried out before the required radiochemical analytical techniques were perfected, and as a result it can be seen (Table

8) that, where the values from duplicate runs were obtained, the agreement is not as good as desired, though it was satisfactory for the purpose of these tests. The solvent used was diethyl ether.

It appears from Table 8 that, up to a fluoride-to-Th(IV) ratio of about unity, HF concentration has little effect on the extraction of either uranyl or thorium; at a ratio of 2 the extraction efficiencies of both these metallic ions are decreased.

4. ON THE MECHANISM OF THE CATALYTIC DISSOLUTION BY FLUORIDE

Essentially nothing is known about the mechanisms of the catalytic effect of HF or fluosilicate on the dissolution of thorium in nitric acid. As mentioned earlier (see Table 1), under a given set of conditions the rate of dissolution was approximately proportional to the first power of the HF concentration.

Hindman and McLane⁶ of the Metallurgical Laboratory of Chicago have evidence for a monofluoride complex of Pu(IV) ion, i.e., PuF^{+3} , with a dissociation constant of the order of 10^{-7} . This evidence was obtained from a study of the absorption spectra in solutions containing fluoride, and these authors believe that complexes involving more than one fluoride per Pu(IV) also exist. Other work at the Metallurgical Laboratory⁷ showed that on adding fluoride to solutions of U(IV) no precipitate was obtained until after 2 moles of fluoride per mole of U(IV) had been added, indicating the existence of the complex UF_2^{++} .

The authors of this paper found similarly that no precipitate was obtained until after 2 moles of fluoride had been added to solutions of Th(IV), again indicating Th(IV)- F^- complexes. Perhaps some sort of thorium-fluoride complex enters into the mechanism of the catalytic dissolution of thorium metal and dioxide.

5. ON OTHER MEDIA FOR THE DISSOLUTION OF Th AND/OR ThO_2

Although HNO_3 -HF and HNO_3 -(NH_4)₂SiF₆ mixtures were found to be satisfactory dissolution media for thorium metal, it was considered desirable to try other media, both out of scientific curiosity and because another mixture might be satisfactory on a large scale. Both perchloric and phosphoric acids were found to attack metallic thorium very slowly. Adding small amounts of H_2SO_4 , $\text{Hg}(\text{NO}_3)_2$, KI, Na_2SO_4 , $\text{Co}(\text{NO}_3)_3$, or $\text{Fe}(\text{NO}_3)_3$ to nitric acid did not noticeably increase the rate of solution of the metal in this acid. Nor did the use of metallic platinum vessels (with the thorium metal contacting the platinum) appear to increase the rate over that obtained in pyrex-glass vessels.

Bohlmann and Kennedy⁸ have reported an apparent increase in solubility in mineral acids of ThO_2 samples after pretreatment with strong NaOH solution.

6. SUMMARY

1. Thorium metal and dioxide have been found to dissolve quite readily in strong HNO_3 containing a small amount of fluoride or fluosilicate.

2. A recommended set of conditions involves concentrated HNO_3 containing 0.05M HF and temperatures near the boiling point.

3. The corrosion rate on heat-treated 25-12 stainless steel under the recommended dissolving conditions is only of the order of 0.0003 in. per month. The corresponding corrosion on tantalum is less than 0.00001 in. per month, i.e., too low for detection.

4. The low concentrations of fluoride in the solutions resulting after dissolution do not affect a subsequent separation of uranium from the dissolved thorium by solvent extraction.

5. The mechanism of the catalytic dissolution of Th or ThO_2 by fluoride may involve complexes of thorium with fluoride.

6. Other media for the dissolution of the metal were tried without success.

Table 1—Dissolution Times for Th and U Metals in Stainless Steel Vessels at Approximately 100°C in 5 Ml of Dissolution Medium

Expt. No.	Metal	Wt., g	Solution for dissolving metal	Time for dissolving
1	Th	0.35	Conc. HNO_3	30 % of metal in 90 min
2	Th	0.70	4N HNO_3	3 % of metal in 90 min
3	Th	0.51	Conc. HNO_3 + 0.1N HF	Complete in 13 min
4	Th	0.48	Conc. HNO_3 + 0.1N HF	Complete in 17 min
5	Th	0.53	Conc. HNO_3 + 0.05N HF	Complete in 21 min
6	Th	0.48	Conc. HNO_3 + 0.012N HF	Complete in 65 min
7	Th	0.46	Conc. HNO_3 + 0.012N HF	Complete in 72 min
8	Th	0.37	Conc. HNO_3 + 0.01M $(\text{NH}_4)_2\text{SiF}_6$	Complete in 20 min
9	Th	2.15	Conc. HNO_3 + 0.05N HF	Complete in 90 min
10*	Th filings	0.38	5 ml 8N HNO_3 + 0.012N HF	Complete in 6 min
11†	U	0.53	Conc. HNO_3	Complete in 30 min

*The temperature of this experiment was about 90°C.

†In this case 7 ml of dissolution medium was used.

Table 2—Dissolution of 0.5-g Samples of ThO_2 in 10 Ml of HNO_3 -HF at 100°C in Pyrex-glass Vessels

HNO_3 normality	HF normality	Time for complete solution, min
8	0.011	11
8	0.0082	13
8	0.0055	15
8	0.0027	Not dissolved in 5 hr
16	0.011	3.5
16	0.0055	3.5
16	0.0027	5

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5	Th	0.53	Conc. HNO_3 + 0.05N HF	Complete in 21 min
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7	Th	0.46	Conc. HNO_3 + 0.012N HF	Complete in 72 min
8	Th	0.37	Conc. HNO_3 + 0.01M $(\text{NH}_4)_2\text{SiF}_6$	Complete in 20 min
9	Th	2.15	Conc. HNO_3 + 0.05N HF	Complete in 90 min
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16	0.0055	3.5
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Table 3—Dissolution of 0.5-g Samples of ThO_2 in 10 ml of HNO_3 - $(\text{NH}_4)_2\text{SiF}_6$ at 100°C in Pyrex-glass Vessels

HNO_3 normality	$(\text{NH}_4)_2\text{SiF}_6$ normality	Time for complete solution, min
16	0.010	9
8	0.010	6
16	0.015	9
8	0.0027	9.5

Table 4—Dissolution of 10-g Samples of ThO_2 in HNO_3 Media (28 ml of 16N in each case)

Sample	Conditions	Time for complete dissolution
a	HF added to 0.05N, and mixture heated in stainless steel beaker at 105 to 110°C	20 min
b	HF added to 0.05N, and mixture heated in pyrex-glass vessel at 100°C	50 min
c	No HF or fluosilicate added, mixture heated in pyrex-glass vessel at 100°C	1.2 per cent dissolved in 50 hr

Table 5—Dissolution of 0.5-g Samples of ThO_2 in 8N HNO_3 - $(\text{NH}_4)_2\text{SiF}_6$ Mixtures

Temp., $^\circ\text{C}$	$(\text{NH}_4)_2\text{SiF}_6$ molarity	Time for complete dissolution
100	0.003	11 min
76	0.003	22 min
50	0.006	Between 2 and 16 hr

Table 6—Corrosion of Heat-treated 25-12 Stainless Steel by HNO_3 -HF and HNO_3 - $(\text{NH}_4)_2\text{SiF}_6$ Mixtures in Presence and Absence of Thorium

Solution composition	Molarity	Temp., °C	Corrosion rates, in./month
HNO_3	16.0	105	0.02
HF	0.1		
HNO_3	16.0	105	0.003
HF	0.1		
$\text{Th}(\text{NO}_3)_4$	0.5		
HNO_3	16.0	105	0.0086
HF	0.01		
HNO_3	16.0	105	0.0016
HF	0.01		
$\text{Th}(\text{NO}_3)_4$	0.05		
HNO_3	7.9	110	0.0001
HF	0.05		
$\text{Th}(\text{NO}_3)_4$	1.5		
HNO_3	10.4	110	0.0004
HF	0.05		
$\text{Th}(\text{NO}_3)_4$	1.9		
HNO_3	13.0	110	0.004 (0.00004 for tantalum)
HF	0.05		
$\text{Th}(\text{NO}_3)_4$	2.4		
HNO_3	16.0	105	0.008
$(\text{NH}_4)_2\text{SiF}_6$	0.003		
HNO_3	8.0	105	0.0015
$(\text{NH}_4)_2\text{SiF}_6$	0.003		
$\text{Th}(\text{NO}_3)_4$	0.5		
HNO_3	8.0	76	0.0002
$(\text{NH}_4)_2\text{SiF}_6$	0.003		
$\text{Th}(\text{NO}_3)_4$	0.5		

Table 7—Corrosion of Heat-treated 25-12 Stainless Steel and of Tantalum by HNO_3 - HF - $\text{Th}(\text{NO}_3)_4$ Mixtures during the Dissolution of Thorium Metal at 110°C

Composition	Solution		Corroded material	Exposure time, hr	Corrosion rate, in./month
	Concentration				
HNO_3	(60-15)%		25-12 stainless steel	29	0.00030
HF	0.05M				
$\text{Th}(\text{NO}_3)_4$	(0.0-3.0)M				
HNO_3	(60-3)%		25-12 stainless steel	21	0.00026
HF	0.05M				
$\text{Th}(\text{NO}_3)_4$	(0.0-6.2)M				
HNO_3	(60-8)%		25-12 stainless steel	26	0.00020
HF	0.05M				
$\text{Th}(\text{NO}_3)_4$	(0.0-3.0)M				
HNO_3	(60-8)%		Tantalum	26	0.00000
HF	0.05M				
$\text{Th}(\text{NO}_3)_4$	(0.0-3.0)M				

Table 8—Effect of HF Concentration on the Separation of Uranium from Thorium by Solvent Extraction into Diethyl Ether from 0.87M $\text{Th}(\text{NO}_3)_4$ -0.83M $\text{Al}(\text{NO}_3)_3$ -1M HNO_3 Aqueous Solution

Mole ratio $\text{HF}/\text{Th(IV)}$	Distribution ratio (ether/solution)	
	Th	U
0	0.23; 0.28	1.8
1	0.22	1.2; 1.9
2	0.145; 0.15	0.53, 0.81

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Paper 7.2

A STUDY OF THE PEROXIDES OF THORIUM

By John W. Hamaker and Charles W. Koch

[Editor's Note: This paper was a contribution from the University of California, Berkeley, and is based on Reports CC-3016 and CC-3770.]

ABSTRACT

Thorium peroxides were prepared in ammoniacal and acid media and from nitrate, sulfate, chloride, and perchlorate solutions. The water-washed solids were analyzed both wet and dry, and analyses were made for sulfate, nitrate, chloride (also chlorine in perchlorate), peroxide oxygen, hydrogen, and thorium. In all cases sulfate, nitrate, chloride, or perchlorate was present in the washed peroxide. The peroxides formed in nitrate, chloride, and perchlorate solutions were quite variable in composition but had very approximately the formula $\text{Th}(\text{O}^-)_{3.2}(\text{A}^-)_{0.5}(\text{O}^{--})_{0.15} \cdot 2.5\text{H}_2\text{O}$, where A^- stands for the anion in question. X-ray powder photographs by Zachariasen of thorium peroxide nitrate showed very poor crystallization, and this characteristic is probably associated with the indefinite composition of the solid. Thorium peroxide sulfate is a definite compound with the formula $\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$. Its x-ray pattern, which was too complex to be analyzed, showed that the material is crystalline.

1. INTRODUCTION

In connection with work of the project, it became desirable to understand the nature of the thorium peroxides that are precipitated when thorium solutions are treated with hydrogen peroxide. Accordingly, a large number of samples were prepared and analyzed; the results are collected in this paper. The peroxides were formed under a

variety of conditions: in alkaline, neutral, and acidic media and in nitrate, sulfate, chloride, and perchlorate solutions.

2. ANALYTICAL PROCEDURE

The precipitated peroxides were washed, in most instances, with water and either analyzed wet or dried and then analyzed. In some cases only a portion of the material was dried, and both wet and dried portions were analyzed. The wet samples were analyzed for peroxide oxygen and for thorium; the dried solids were analyzed for residue (ThO_2), hydrogen, peroxide oxygen, sulfate, chloride, and nitrate, whichever constituents were present.

2.1 Analyses of Washed, Undried Precipitates. The peroxide content of the wet material was determined either by direct titration in acid solution with potassium permanganate or by the addition of excess ceric ion and back-titration with ferrous ammonium sulfate using ferroin (*o*-phenanthroline-ferrous complex) as an indicator. The solution resulting from the peroxide oxygen determination was then analyzed for thorium. Where permanganate was used in the peroxide titration, thorium was precipitated as the oxalate by the addition of excess oxalic acid, washed free from manganous ion, and ignited to ThO_2 . In the four instances where cerium and iron were present from the analysis for peroxide oxygen, the phenyl arsonate separation procedure was used.¹ In all other cases where the cerium titration had been employed, the supernatant solution and washings from the precipitated thorium peroxide were saved, and thorium oxalate or hydroxide was precipitated from them. The total thorium used was carefully measured, and the thorium in the peroxide was thus determined by difference. Because of the difficulties of microgravimetric analyses, this work was done on a macro scale. This is in contrast to the combustion analyses which employed a microanalytical technique.

2.2 Combustion Analyses of Dry Peroxides. In the combustion analyses of the dry material, hydrogen, residue (ThO_2), sulfate, and chloride were determined simultaneously using a modified micro carbon-hydrogen apparatus.² The sulfate and chloride determinations were adapted from the procedure of Belcher and Spooner³ in which sulfur and chloride are caught on silver gauze as silver sulfate and silver chloride.

The nitrate content was determined by means of the micro Dumas apparatus using a carbon-hydrogen combustion tube instead of the ordinary Dumas tube. The sample was introduced in a platinum boat and was not subjected to the usual procedure of mixing with powdered copper oxide since no oxidation was necessary. For the same

reason a packing of reduced copper replaced the standard packing of coarse copper oxide and reduced copper. Nitrogen analyses on lead nitrate using this method gave nitrogen concentrations of 8.40 and 8.41 per cent (theoretical, 8.45 per cent).

The peroxide oxygen in most dry thorium peroxides was determined by the addition of an excess of ceric ion and back-titration with ferrous ion using ferroin as an indicator. Only thorium peroxide chloride was sufficiently reactive to permit direct titration with potassium permanganate. A dry combustion method for peroxide oxygen content was also devised. It employs the same apparatus as described above for the nitrogen determination, but it uses no packing in the combustion tube. By this method the oxygen given off on heating the sample is collected and measured in a microazotometer. Nitrate does not interfere with this method, and peroxide chlorides have been run successfully; but when sulfate is present care must be taken not to overheat, since the reaction $\text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2}\text{O}_2$ will take place, thus yielding a high peroxide oxygen value. The sulfate is quite tenaciously held, whereas the peroxide will decompose at a relatively low temperature. The peroxide content of thorium peroxide perchlorate cannot be determined by this procedure because the perchlorate is not sufficiently stable. In Table 1 are listed the percentages of peroxide oxygen for a thorium peroxide nitrate and a thorium peroxide sulfate as determined by both the wet and dry methods. The estimated maximum deviations for the above-described methods of analysis are: H, Cl, S, N, and peroxide oxygen, ± 2 per cent; ThO_2 , ± 1 per cent. These are relative per cents, e.g., if a sample is reported to contain 15.0 per cent nitrogen, the true value should lie between 14.7 and 15.3 per cent.

3. THORIUM PEROXIDE NITRATE PRECIPITATED FROM AMMONIACAL SOLUTION

Many of the peroxides of thorium that are reported in the literature were formed from ammoniacal solutions;⁴ thus the first series of peroxides was prepared in ammoniacal media. The general procedure was as follows: A dilute solution of thorium nitrate and of hydrogen peroxide was cooled to 0°C and made alkaline with ammonia. The gelatinous precipitate which formed immediately on the addition of base was washed very thoroughly with ice water (12 times) and dried by exposing to high vacuum. The results from analyses of these preparations are given in Table 2 together with the conditions of formation. Residue (ThO_2), hydrogen, and peroxide oxygen were determined directly. Nitrate and oxide oxygen contents were calculated on the

assumption that only those two constituents were present in addition to the ones determined.

It is possible to represent peroxide oxygen in one of two ways, namely, as equivalents of peroxide oxygen or as moles of active oxygen. This latter designation is almost universally used in the literature and essentially means moles of nascent oxygen as formed in the hypothetical reaction $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$. In this case active oxygen represents two equivalents of oxidizing power per mole, but no indication is given of reducing power by such a nomenclature. Moreover, it does not show the charge associated with peroxide ion. For these reasons this nomenclature was not used, and peroxide oxygen content has been expressed in terms of the number of peroxide oxygen atoms per mole of metal. This is equal to the number of equivalents of peroxide oxygen or twice the number of moles of peroxide per mole of metal. The formula Th_2O_7 , therefore would have three equivalents of peroxide oxygen per thorium, which means that three of the plus charges of thorium are satisfied by peroxide oxygen atoms and there is one-half an oxide oxygen atom needed to fully neutralize the thorium, i.e., $2\text{Th}(\text{O}^-)_3(\text{O}^{--})_{1/2}$. In writing the formula in this manner it is not meant that O^{--} is actually present in the compound; the peroxide is undoubtedly in the form of two oxygens linked together, i.e., OO^{--} .

Similarly, the hydrogen and oxide oxygen present in the compound can be represented in two ways. They can be written in the formula as separate constituents or combined to form water. Thus the formula $\text{Th}(\text{O}^-)_{2.10}(\text{NO}_3^-)_{0.40}(\text{O}^{--})_{1.93}(\text{H}^+)_{2.36}$ is equivalent to the formula $\text{Th}(\text{O}^-)_{2.10}(\text{NO}_3^-)_{0.40}(\text{O}^{--})_{0.75} \cdot 1.18\text{H}_2\text{O}$, and it is completely arbitrary as far as the analyses are concerned as to which formula is chosen to represent the composition of the compound. In the calculations for this report, as much as possible of the H^+ and O^{--} were combined to form water in the manner shown by the second formula. This does not mean, of course, that the hydrogen is necessarily present in the compound as water. Also, the peroxide groups have been represented as having no hydrogen ions attached, but this is only an arbitrary representation.

No analyses were made for ammonium ion. However, it should be noted that the presence of ammonium ion would raise the hydrogen content very markedly. The hydrogen-to-thorium ratio was actually found to be lower for these compounds than for similar compounds precipitated from neutral and acid solutions (Tables 3 and 4) where ammonium ion was not present.

In addition to the washing procedure given above, an attempt was made to wash with alcohol and ethyl ether after washing with water. The material thus obtained could not be freed of carbon (several

per cent) by exposure to high vacuum for 2 hr or by exposure to air for as long as several days. Schwarz and Giese⁴ report a similar effect with zirconium peroxide and petroleum ether, acetone, and methanol. For these reasons all organic washes were excluded in this work.

An examination of Table 2 will disclose that the peroxide content varies erratically but depends to some extent on the severity of the drying treatment. The two samples that were air-dried (2 and 9 days, respectively) contain definitely more peroxide oxygen as well as more hydrogen than the samples that were vacuum-dried. There is little difference in peroxide oxygen content between the samples dried on high vacuum for 16 hr and those dried on high vacuum for 60 hr. The single sample dried on house vacuum over calcium chloride is not in agreement with the other results since the peroxide oxygen content is lower but the hydrogen content is not. It should be pointed out that the water content reported is not the minimum water content achieved but represents the state of hydration when at equilibrium with the atmosphere. All these peroxides pick up water when exposed to air after vigorous drying, and they were allowed to come to equilibrium with the air before analysis. This was necessary since, for analysis, the material was weighed out into open combustion boats. The calculated nitrate content of the samples varies quite markedly.

4. THORIUM PEROXIDE NITRATES PRECIPITATED FROM "NEUTRAL" SOLUTION

The next series of thorium peroxide nitrates was formed from neutral solution. A dilute solution of thorium nitrate was treated with hydrogen peroxide and either heated or allowed to stand to bring down the gelatinous peroxide. This peroxide is far more gelatinous than that formed in ammoniacal solution, and in several cases the entire solution set into a gel. As before, the material was washed with water very thoroughly (12 times) and dried. The data for this series are summarized in Table 3.

Compared with peroxides obtained from ammoniacal solution, these samples contain more peroxide oxygen (about 2.9 peroxide oxygen atoms per Th instead of about 2), and at equilibrium with atmospheric water vapor they contain more hydrogen (about 4.4 H per Th instead of about 2.4). Even when vacuum-dried and stored at room temperature, these compounds are found to decompose slowly, losing about 10 per cent of their peroxide oxygen in 1 week. The nitrate content is much more uniform than before, indicating that the

fluctuation in the first series is real, since in both instances the nitrate content was calculated rather than determined directly. There seems to be roughly 0.5 nitrate ion for each thorium.

5. THORIUM PEROXIDE NITRATE PRECIPITATED FROM ACID SOLUTION

Next a series of peroxides was prepared in acid media. When formed under these conditions, the thorium peroxide is compact and white instead of gelatinous and transparent. When formed at elevated temperature, the individual particles are well-formed pellets which give a suggestion of some structure. Washing with water appears to break up these particles to some extent. The results for this series of compounds are presented in Table 4.

Nitrate is present to the extent of about half an ion per thorium atom, and the experimental values stay quite close to that ratio. However, the experimental error in the analyses is estimated at ± 2 per cent (see Sec. 2.2), and values do vary from 0.50 by more than this per cent. With the exception of four samples, all peroxide oxygen contents lie between the limits of 3.22 and 3.14 atoms per atom of thorium. This constancy held (within 3 per cent) although the precipitation conditions varied very widely: 2.0M to 0.5M H^+ , 3.3M to 0.4M H_2O_2 , and room temperature to $100^\circ C$. The four samples (4, 5, 6, and 7) contained less peroxide and differed from the others in that they were washed with 3 per cent hydrogen peroxide instead of water. Possibly the hydrogen peroxide present during the drying process set up a catalytic mechanism for decomposition because the material slowly evolved a pungent gas, probably NO_2 or O_3 . This gas was not noted in any other samples. In this connection it is significant to note that Pissarjewsky^{5,6} reported the evolution of ozonized oxygen when thorium peroxide was treated with concentrated sulfuric acid. This was true when the peroxide was prepared from nitrate solution or from sulfate solution, which would seem to indicate that ozone was being evolved and not NO or NO_2 . Pissarjewsky mentions no special test for ozone, so he probably judged from the odor.

In about one-half the samples a determination was made of the water take-up during exposure to air following drying. It is interesting to note that the dry material contains 1.5 water molecules per thorium. In view of the vigorousness of the drying conditions, it does not seem likely that this residual water could be removed without decomposing some of the peroxide oxygen in the compound. It will be recalled that in the case of peroxides formed from ammoniacal solutions the water

content after exposure to air was lower than corresponding values in this series but that the peroxide oxygen content was also lower.

It was of interest to know the peroxide oxygen content of the washed, undried precipitates. A large number of peroxides were prepared, washed liberally with water, and analyzed wet. The results are reported in Table 5. Four of these peroxides (samples 8, 9, 10, and 11) have already been reported (Table 4) as the dry compounds since a portion of the washed precipitates had been removed, dried, and analyzed. In these four cases the peroxide content of the wet material was higher than, or at least equal to, that of the dry material and was also more variable (6.5 per cent maximum deviation as compared with 1.3 per cent maximum deviation).

Conditions were widely varied in an attempt to get a peroxide content as high as possible. The limit under the conditions tried appears to be 3.5, but it is difficult to get a value that high. Most peroxide values fall below that mark. Even when conditions are duplicated, peroxide values will vary widely (see samples 14 and 15, Table 5). High peroxide oxygen values occur for hydrogen peroxide concentrations from 3.3M to 0.1M. The washing of the precipitates was thorough, and in view of the relatively compact nature of the precipitates it is felt that the results do not vary because of hydrogen peroxide holdup but because of actual variations in the nature of the precipitates. These variations may occur during washing or during precipitation or during both processes. It is of interest to note that, if peroxide oxygen is present to the extent of 3.5 atoms per thorium and there is 0.5 nitrate per thorium, the thorium charge of +4 is completely satisfied.

6. THORIUM PEROXIDE SULFATE

The last three samples in Table 5, precipitated in the presence of sulfuric acid, represent an entirely different type of compound, as is indicated by the peroxide-to-thorium ratio of 2.0. The solid is quite dense and so stable that it requires prolonged heating with excess ceric solution to decompose it (20 to 30 min). This peroxide usually requires heating to precipitate it, which is not generally true of the peroxides precipitated from nitric acid (also hydrochloric or perchloric acid). Samples of the solid were prepared, dried, and analyzed; and the results are presented in Table 6. The analyses correspond closely to the formula $\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$. The peroxide-to-thorium ratio is the same for wet and dried material, so there is no decomposition during drying. In this regard it is interesting to note the tenacity with which the three water molecules are held in the compound.

7. THORIUM PEROXIDE CHLORIDE AND THORIUM PEROXIDE PERCHLORATE

Thorium peroxide chloride is definitely unstable. In the three samples which were prepared a strong odor of chlorine accumulated in the container when the material was allowed to stand. From Table 7, where data on these samples are presented, it will be seen that the peroxide oxygen content drops at about the same rate as in samples 1 and 2, Table 3, over a period of 1 week. The thorium peroxide perchlorate results are also presented in Table 7. This compound does not liberate chlorine as far as could be detected.

8. DISCUSSION

A summary of the thorium peroxides reported in the literature is given in Table 8. From an examination of the table it will be evident that the formula Th_2O_7 , usually written for thorium peroxide, is incorrect. Although it is a very approximate representation of the usual peroxide oxygen content (three equivalents of peroxide oxygen per thorium atom), it omits the anion that is associated with the compound.

The first report of thorium peroxide nitrate by Wyruboff and Verneuil states definitely that nitrate was present in the compound, and later work by Calzolari also shows the presence of nitrate. Schwarz and Giese, however, ignore nitrate completely and hence count it as water which they determined by difference. Pissarjewsky makes the unsupported statement that there was no nitric acid in the peroxide obtained from neutral solution of thorium nitrate. Under the same conditions in the experiments reported here approximately 0.5 nitrates per thorium were found consistently in the washed and dried peroxide. This value of 0.5 is lower than the value of 1 reported by Wyruboff and Verneuil, but these authors give no information as to the method of precipitation nor as to the method of analysis of the single sample. The value of 1.0 nitrate per thorium reported by Calzolari represents the nitrate content of the unwashed precipitate. This work would seem to require checking before it can be relied upon; but if it is correct it would indicate that nitrate is removed during the washing process, about one-half of it being washed out. This might explain why the nitrate values that were obtained in the studies reported in this paper are somewhat variable.

The method employed by Calzolari to arrive at the composition of precipitated thorium is rather unique. A solution containing a known weight of thorium was treated with an accurately determined excess of hydrogen peroxide. The supernatant solution was analyzed to de-

termine the unconsumed hydrogen peroxide and also the acid liberated in the formation of thorium peroxide. It was assumed that the thorium peroxide precipitates completely. The ratio of peroxide oxygen to thorium was then calculated from the peroxide oxygen analysis. The maximum amount of acid formed is four hydrogen ions per thorium, and this is diminished if any anion such as nitrate is present in the peroxide precipitate, e.g.,

The anion (nitrate, sulfate, etc.) content can therefore be calculated from the acidity of the supernatant solution. Calzolari analyzed his thorium salts so that he knew them to be neutral salts or could, in the case of the chloride, apply a correction for an admixture of basic salt. In the case of thorium nitrate he found an excess of nitrate which he assumed was due to nitric acid. If, instead, this excess was due to error in nitrate analysis or to the presence of a neutral nitrate salt, his data represent 0.85 nitrate per thorium atom instead of 1.0. He worked at low temperatures, 4 to 5°C, to minimize the decomposition of hydrogen peroxide, and he states that over a period of 15 hr there was no significant loss of peroxide oxygen. He did not check the assumption that thorium peroxide is quantitatively precipitated; but if any thorium did not precipitate he should have observed a gelatinous precipitate when titrating the supernatant solution with KOH. In the studies reported here the precipitate was observed to form before reaching a methyl red end point. Calzolari added considerable neutral salt (such as ammonium nitrate) with the hydrogen peroxide, and this probably ensured quantitative separation of thorium peroxide by coagulating any colloid. Thorium peroxide has a considerable tendency to form a colloid, as shown by the readiness with which it peptizes when washed with water. If any thorium did not precipitate, the ratio of peroxide oxygen to thorium would have been low.

The composition of thorium peroxide nitrate shows a definite variation with the acidity at the time of precipitation. In the work reported in this paper some samples of thorium peroxide were precipitated by adding ammonia to a thorium nitrate solution which contained hydrogen peroxide. When washed and dried, these samples contained approximately 2 peroxide oxygens per thorium and between 0.14 and 0.72 nitrate per thorium (see Table 2). The composition of the dry peroxides prepared by the above procedure is not reproducible. It is not known whether the variation occurs in the precipitation, the washing, or the drying treatment. There are no

references in the literature to thorium peroxide nitrates formed in ammoniacal solution.

The samples of washed and dried thorium peroxide nitrate, given in Table 3, contain roughly 3 peroxide oxygens and 0.5 nitrate per thorium atom. These were prepared by adding hydrogen peroxide to a solution of thorium nitrate. This solution is initially low in acid, but as the precipitation proceeds the acidity increases owing to the liberation of H^+ in the formation of the solid. Pissarjewsky and Calzolari both precipitated the peroxide under these conditions. They found between 3.0 and 3.3 peroxide oxygen atoms per thorium. Their samples were analyzed wet, and, since the peroxide content they found was somewhat higher than reported here, this may again indicate some decomposition of peroxide oxygen on drying. However, if the washing treatment used in this investigation was more severe than that employed by Pissarjewsky, more peroxide may have been removed in washing. Schwarz and Giese found 2.9 peroxide oxygens per thorium in a similarly prepared sample that was dried with liquid ammonia. In view of the presence of ammonia in the compound, it is difficult to interpret this result.

Calzolari reported 1.0 nitrate per thorium in the above compound, which is higher than the value of roughly 0.5 reported in Table 3. Calzolari's method of analysis should yield the composition of the unwashed material, and this difference may indicate loss of nitrate from the compound on washing and drying.

There are no results reported in the literature concerning the precipitation of thorium peroxide nitrate from solutions initially containing nitric acid. The analyses given in Table 5 show a composition of 3.16 to 3.53 peroxide oxygens per thorium in the wet, water-washed precipitates. In Table 4 the dried material contains 2.91 to 3.22 peroxide oxygens and 0.5 nitrate per thorium. The composition is variable.

In the literature the peroxides prepared from thorium sulfate do not correspond to $Th(OO)SO_4 \cdot 3H_2O$, reported in this work, which has a peroxide oxygen-to-thorium ratio of 2. Thorium peroxides prepared in sulfate solutions by various investigators contain more nearly 3 peroxide oxygens per thorium. Sulfate contents of 0.46, 0.44, and 0.00 sulfates per thorium reported by Calzolari and by Cleve do not correspond to $Th(OO)SO_4 \cdot 3H_2O$. The reason for this lack of correspondence is that the peroxide sulfates reported in the literature were formed in weakly acid or ammoniacal solution. In work discussed in another paper in this volume⁷ it was found that thorium peroxides precipitated from weakly acid sulfate solutions were quite different from $Th(OO)SO_4 \cdot 3H_2O$ in behavior and composition. These peroxides correspond to the thorium peroxide sulfates reported in the literature.

The thorium peroxide chlorides prepared by Calzolari contain somewhat less chloride than those listed in Table 8. This may possibly be due to the rather incomplete washing which was necessitated by the extreme tendency of the precipitate to peptize when washed with water; but it should be pointed out that conditions of precipitation differed in that Calzolari prepared his peroxides from a thorium chloride solution containing some basic chloride whereas the peroxide chlorides in Table 8 were prepared from a solution 1M in hydrochloric acid. The peroxide contents of the dry samples in Table 8 are somewhat lower than peroxide contents in Calzolari's samples, which were wet.

There are no reports in the literature of thorium peroxide perchlorate. The one sample given in Table 8 is the same general type of compound as thorium peroxide chloride.

In connection with the tendency of all thorium peroxides to peptize when washed with water [$\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$ is an exception], it is interesting to note that Calzolari was able to produce a colloid of thorium peroxide chloride. By dialyzing the material he was able to remove practically all the chloride without greatly changing the ratio of peroxide oxygen to thorium. After 10 days dialysis, 0.26 chloride and 3.0 peroxide oxygens were present per thorium, and after 50 days dialysis, 0.03 chloride and 2.9 peroxide oxygens were present. Therefore chloride apparently can be removed from the material while the peroxide is firmly held by the thorium. Possibly colloids could be produced from thorium peroxide nitrate and perchlorate solutions, and it would be interesting to see if the anion could be removed by dialysis. In fact, from the tendency to peptize, it might be expected that, if a solid thorium peroxide nitrate, chloride, or perchlorate were water-washed by dialysis, the material would peptize completely to yield a colloidal solution. It would seem that this colloidal behavior of thorium peroxide should be investigated further since there are many indications of colloidal effects in the behavior of the thorium peroxide system.

9. X-RAY PATTERNS

We are indebted to Professor Zachariasen for taking x-ray powder photographs of several of the thorium peroxide preparations reported here. He found⁷ that $\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$ gave a pattern of sharp lines indicating a well-crystallized, definite compound, and this conclusion is in agreement with the consistency of the analytical results. The pattern was too complex to be interpreted from a powder photograph.

The thorium peroxide nitrate samples submitted for x-ray analysis were precipitated from nitric acid solution. Zachariasen⁸ reports

that the compound is very poorly crystallized. He states: "Only a few broad diffraction lines occur. These lines seem to correspond to a two-dimensional hexagonal lattice." The poor crystallization is in agreement with the fact that the composition of this solid was found to be irreproducible even under what were believed to be identical conditions of precipitation.

The variability in the nitrate, peroxide, and oxide oxygen content of thorium peroxide nitrate samples (precipitated from nitric acid solution) would indicate that these ions are capable of replacing each other at certain positions in the crystal lattice. Starting with Zachariasen's interpretation of the x-ray data, the compound might then be visualized in terms of a two-dimensional hexagonal lattice containing only peroxide and thorium, perhaps in the ratio of 3 peroxide oxygen atoms to each thorium atom. This lattice would provide the structural framework of the compounds. The two-dimensional lattices would then have their excess positive charges neutralized by any of several negative ions, i.e., NO_3^- , O^{--} , OH^- , OOH^{--} , OO^{--} (also H_2O could be attached). The absence of any x-ray pattern corresponding to structure in a direction perpendicular to these planes indicates that the planes are not bonded to each other in any regular fashion. According to the above picture, this compound of thorium peroxide consists of sheets composed of thorium and peroxide, with negative ions, whose identity is readily varied, attached to the surface of the sheets.

Table 1 — Peroxide Analyses by Wet and Dry Methods

Thorium peroxide	Peroxide oxygen, %	
	Wet method	Dry method
Nitrate	14.31	14.38; 14.56; 14.36
Sulfate	7.75	7.74; 7.72

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Table 2—Thorium Peroxides Precipitated by Making a Solution of Thorium Nitrate and Hydrogen Peroxide Alkaline with Ammonia

Sample	Initial [Th ⁴⁺], moles/ liter	Initial [H ₂ O ₂], moles/ liter	Initial [NH ₃], moles/ liter	Approx. final [NH ₃], moles/ liter*	Drying conditions	ThO ₂ , %	H, %	Peroxide oxygen, %	Formula calculated
1	0.12	0.8	0.48	0.05	16 hr on high vacuum	81.52	0.73	10.44	Th(O ⁻) _{2.10} (NO ₃ ⁻) _{0.46} (O ⁻) _{0.75} ·1.18H ₂ O
2	0.12	0.8	0.48	0.02	48 hr on house vacuum over CaCl ₂	82.94	0.98	7.08	Th(O ⁻) _{1.41} (NO ₃ ⁻) _{0.15} (O ⁻) _{1.22} ·1.56H ₂ O
3	0.12	0.8	0.48	0.09	9 days air-dried	69.85	1.55	10.29	Th(O ⁻) _{2.44} (NO ₃ ⁻) _{0.72} (O ⁻) _{0.42} ·2.94H ₂ O
4	0.0148	0.24	0.135	0.078	16 hr on high vacuum	84.47	0.84	9.74	Th(O ⁻) _{1.90} (NO ₃ ⁻) _{0.14} (O ⁻) _{0.98} ·1.31H ₂ O
5	0.0148	0.24	0.135	0.081	2-3 days air-dried	71.45	2.04	9.50	Th(O ⁻) _{2.19} (NO ₃ ⁻) _{0.38} (O ⁻) _{0.72} ·3.74H ₂ O
6	0.0148	0.24	0.135	0.079	60 hr on high vacuum	85.46	0.74	9.34	Th(O ⁻) _{1.80} (NO ₃ ⁻) _{0.22} (O ⁻) _{0.99} ·1.02H ₂ O
7	0.0148	0.24	0.135	0.080	60 hr on high vacuum	84.05	0.78	8.76	Th(O ⁻) _{1.72} (NO ₃ ⁻) _{0.26} (O ⁻) _{1.01} ·1.23H ₂ O
8	0.0148	0.24	0.135	0.081	60 hr on high vacuum	81.99	0.75	10.11	Th(O ⁻) _{2.04} (NO ₃ ⁻) _{0.37} (O ⁻) _{0.80} ·1.21H ₂ O

*In the reaction between Th⁴⁺ and H₂O₂, H⁺ is liberated, neutralizing some of the NH₃.

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Table 3—Thorium Peroxides Precipitated from "Neutral" Solution Containing Nitrate

Sample	Initial [Th ⁴⁺], moles/ liter	Initial [H ₂ O ₂], moles/ liter	Final [H ⁺], moles/ liter*	Precipitating conditions	Drying conditions	ThO ₂ , %	H, %	Peroxide oxygen, %	Formula calculated
1	0.0146	0.477	0.049	Room temp overnight	42 hr on high vacuum	75.34	0.99	13.16	Th(O ⁻) _{2.89} (NO ₃ ⁻) _{0.66} (O ⁻) _{0.23} ·1.74H ₂ O
1†						74.96	1.18	11.87	Th(O ⁻) _{2.81} (NO ₃ ⁻) _{0.55} (O ⁻) _{0.42} ·2.08H ₂ O
2	0.015	0.244	0.051	Heated to 60° C to ppt, allowed to cool slowly	42 hr on high vacuum	73.84	1.15	13.46	Th(O ⁻) _{3.02} (NO ₃ ⁻) _{0.80} (O ⁻) _{0.19} ·2.06H ₂ O
2†						72.05	1.35	12.20	Th(O ⁻) _{2.80} (NO ₃ ⁻) _{0.66} (O ⁻) _{0.27} ·2.48H ₂ O
3	0.18	1.43	0.53	Room temp overnight	16 hr on high vacuum	74.59	1.34	12.68	Th(O ⁻) _{2.81} (NO ₃ ⁻) _{0.46} (O ⁻) _{0.37} ·2.37H ₂ O
4	0.202	0.32	0.70	Room temp overnight	16 hr on high vacuum	73.84	1.25	12.91	Th(O ⁻) _{2.89} (NO ₃ ⁻) _{0.56} (O ⁻) _{0.26} ·2.22H ₂ O
5	0.202	0.32	0.71	60° C for 1 hr	16 hr on high vacuum	74.52	1.28	13.15	Th(O ⁻) _{2.92} (NO ₃ ⁻) _{0.49} (O ⁻) _{0.30} ·2.26H ₂ O

*In the reaction between Th⁴⁺ and H₂O₂, H⁺ is liberated

†Second analysis performed after sample was exposed to air for 1 week

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Table 4—Thorium Peroxides Precipitated from Nitric Acid
(Dried on high vacuum for 16 hr and analyzed after equilibrium established with water vapor in air)

Sample	Initial [Th ⁴⁺], moles/ liter	Initial [H ₂ O ₂], moles/ liter	Final [H ⁺], moles/ liter	Precipitating conditions	ThO ₂ , %	H, %	Peroxide oxygen, %	NO ⁻³ , %	SO ₄ ⁻² , %	Formula calculated	Change in weight due to H ₂ O uptake in air, %	H ₂ O/Th ⁴⁺ , dry
1	0 0513	3 33	2 0	Room temp , separated immediately	71 44	1 39	13 63			Th(O ⁻) _{3 15} (NO ₃ ⁻) _{0 33} (O ⁻) _{0 11} 2 58H ₂ O		
2	0 021	3 33	2 0	40° C for 2 hr	75 09	1 26	14 40			Th(O ⁻) _{3 17} (NO ₃ ⁻) _{0 42} (O ⁻) _{0 21} 2 21H ₂ O		
3	0 021	3 33	2 0	40° C for 2 hr	75 41	1 15	14 48			Th(O ⁻) _{3 17} (NO ₃ ⁻) _{0 45} (O ⁻) _{0 19} 2 02H ₂ O		
4	0 021	3 33	2 0	100° C for 2 hr, washed with 3 % H ₂ O ₂	72 66	1 46	12 98	9 11		Th(O ⁻) _{2 96} (NO ₃ ⁻) _{0 55} (O ⁻) _{0 35} 2 74H ₂ O (0 49 calc)		
5	0 021	3 33	2 0	80° C for 2 hr, washed with 3 % H ₂ O ₂	73 07	1 48	13 21	7 13		Th(O ⁻) _{2 96} (NO ₃ ⁻) _{0 45} (O ⁻) _{0 29} 2 75H ₂ O (0 44 calc)		
6	0 021	3 33	2 0	60° C for 2 hr, washed with 3 % H ₂ O ₂	73 82	1 39	13 26	6 65		Th(O ⁻) _{2 96} (NO ₃ ⁻) _{0 40} (O ⁻) _{0 32} 2 60H ₂ O (0 43 calc.)		
7	0 021	3 33	2 0	40° C for 2 hr, washed with 3 % H ₂ O ₂	73 30	1 44	12 92	7 30		Th(O ⁻) _{2 91} (NO ₃ ⁻) _{0 43} (O ⁻) _{0 33} 2 68H ₂ O (0.46 calc.)		
8*	0 022	0 64	0 44	Room temp overnight	72 75	1 37	13 99	8 50		Th(O ⁻) _{3 18} (NO ₃ ⁻) _{0 50} (O ⁻) _{0 18} 2 49H ₂ O	4 78	1 50
9*	0 05	0 40	0 5	Room temp overnight	73 69	1 29	14 12	8 24		Th(O ⁻) _{3 16} (NO ₃ ⁻) _{0 48} (O ⁻) _{0 18} 2 31H ₂ O	4 07	1 47
10*	0 05	0 40	0 5	Heated to 90°C, held for 2 hr	72 71	1 36	14 10	8 59*		Th(O ⁻) _{3 20} (NO ₃ ⁻) _{0 51} (O ⁻) _{0 15} 2 48H ₂ O	4 07	1 62
11*	0 05	0 40	0 5	Heated to 90°C, held for 2 hr	72 45	1 27	14 05	8 64		Th(O ⁻) _{3 20} (NO ₃ ⁻) _{0 51} (O ⁻) _{0 15} 2 31H ₂ O	3 90	1 49

*The wet analyses for samples 8, 9, 10, and 11 are found in Table 5

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Table 4—(Continued)

Sample	Initial [Th ⁺⁺], moles/ liter	Initial [H ₂ O ₂], moles/ liter	Final [H ⁺], moles/ liter	Precipitating conditions	ThO ₂ , %	H, %	Peroxide oxygen, %	NO ₃ ⁻ , %	SO ₄ ⁻ , %	Formula calculated	Change in weight due to H ₂ O uptake in air, %	H ₂ O/Th ⁺⁺ , dry
12	0.04†	1.6	0.64	Room temp for 1 hr, heated to 70° C, stirred 1½ hr at 70° C	72.47	1.44	14.01			Th(O ⁻) _{3.19} (NO ₃ ⁻) _{0.51} (O ⁻) _{0.15} 2.63H ₂ O		
13	0.038†	1.92	0.62	Room temp for 1 hr, diluted, heated at 40° C for 1 hr	73.40	1.39	14.07			Th(O ⁻) _{3.18} (NO ₃ ⁻) _{0.47} (O ⁻) _{0.19} 2.50H ₂ O		
14	0.156	0.73	0.94	H ₂ O ₂ added over 1 hr at 70° C, di- gested 3 hr at 70° C†	73.54	1.31	14.31	7.75	0.21	Th(O ⁻) _{3.22} (NO ₃ ⁻) _{0.45} (SO ₄ ⁻) _{0.01} (O ⁻) _{0.18} 2.36H ₂ O	4.05	1.55
15	0.156	0.73	0.94	Room temp overnight‡	72.97	1.38	13.95	8.32	0.00	Th(O ⁻) _{3.18} (NO ₃ ⁻) _{0.49} (SO ₄ ⁻) _{0.00} (O ⁻) _{0.18} 2.50H ₂ O	4.79	1.54
16	0.156	0.73	0.94	Room temp overnight‡	73.24	1.34	13.92	7.71	0.00	Th(O ⁻) _{3.14} (NO ₃ ⁻) _{0.45} (SO ₄ ⁻) _{0.00} (O ⁻) _{0.21} 2.42H ₂ O	4.56	1.50

†The stock solution consisted of 1M Th⁺⁺ in 16M HNO₃.‡The stock solution of Th⁺⁺ was precipitated as the hydroxide twice and redissolved in HNO₃.

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Table 5 — Analyses of Wet Thorium Peroxide Precipitates Formed in Acid Solution

Sample	Initial [Th ⁴⁺], moles/ liter	Initial [H ₂ O ₂], moles/ liter	Final [HNO ₃], moles/ liter	Final [H ₂ SO ₄], moles/ liter	Precipitating conditions	O ⁻ /Th ⁴⁺
1	0.177	0.268	0.92		Room temperature for 2 hr	3.20
2	0.079	0.109	0.66		H ₂ O ₂ added over 2 hr, stirred over- night at 40°C	3.30
3	0.091	0.151	0.78		All H ₂ O ₂ added at once, stirred over- night at room temperature	3.53
4	0.074	0.124	0.63		Heated to 100°C and stirred 2 hr	3.52
5	0.074	3.7	0.05		Hydroxide precipitated, then H ₂ O ₂ added and stirred overnight at 0°C	3.18
6	0.074	0.124	0.62		Heated to 40°C and stirred overnight	3.37
7	0.167	3.3	0.89		Precipitated rapidly, washed im- mediately	3.34
8*	0.022	0.64	0.44		Stirred at room temperature overnight	3.21
9*	0.05	0.40	0.5		Stirred at room temperature overnight	3.16
10*	0.05	0.40	0.5		Heated to 90°C and stirred for 2 hr	3.37
11*	0.05	0.40	0.5		Heated to 90°C and stirred for 2 hr	3.29
12	0.0166	3.94	0.45		Stirred 0°C overnight, precipitated within 1st hr	3.27
13	0.074	3.72	0.66		Precipitated rapidly, digested at 40°C overnight	3.49
14	0.077	0.31	0.64		Stirred at 40°C for 42 hr	3.26
15	0.077	0.31	0.65		Stirred at 40°C for 42 hr	3.45
16	0.163	3.3	0.87		Stirred at 40°C overnight†	3.44
17	0.163	3.3	0.87		Stirred at 40°C overnight†	3.42
18	0.187	0.44	1.61		Stirred at room temperature overnight†	3.27
19	0.187	0.44	1.61		Stirred at room temperature overnight†	3.25
20	0.137	2.76	0.70		H ₂ O ₂ added at 70°C over 1 hr, stirred at 70°C for another 2 hr	3.29
21	0.137	2.76	0.70		Same	3.29
22	0.143	2.95	0.78		H ₂ O ₂ added at room temp. over 1 hr, stirred for 40 hr at room temp.	3.44
23	0.143	2.95	0.78		Same	3.46
24	0.143	2.95	0.75		Same	3.27
25	0.143	2.95	0.76		Same	3.28
26	0.143	2.95	0.75		Same	3.25
27	0.143	2.95	0.75		Same	3.25
28	0.2	8.0	3.12		H ₂ O ₂ added, stirred at 75-80°C for 3 hr†	3.26
29	0.2	8.0	3.12		Same	3.26
30	0.074	0.124	0.328	0.093	H ₂ O ₂ added slowly, stirred overnight at 50°C	1.93
31	0.074	0.124	0.147	0.185	Same	1.99
32	0.074	0.124	0.148	0.185	Heated to 100°C and stirred for 2 hr	1.995

*These are samples 8, 9, 10, and 11 of Table 4.

†The Th⁴⁺ was evaporated with concentrated HNO₃ before H₂O₂ was added

‡Thorium hydroxide was precipitated, washed, and redissolved in nitric acid.

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Table 6 — Analyses of Thorium Peroxide Sulfate $[\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}]^*$

Sample	Initial [Th ⁺⁺], moles/ liter	Initial [H ₂ O ₂], moles/ liter	Initial [HNO ₃], moles/ liter	Initial [H ₂ SO ₄], moles/ liter	Precipitating conditions	ThO ₂ , %	H, %	Peroxide oxygen, %	SO ₄ ⁻ , %	Formula calculated	H ₂ O uptake on exposure to air	H ₂ O/Th in dry compound	O ⁻ /Th ⁺⁺ , wet
1	0.21	3.3	0.5	0.25	Heated to 40° C; H ₂ O ₂ added; heated to 67° C†	63.91	1.58	7.64		$\text{Th}(\text{O}^-)_1{}_{96}(\text{SO}_4^-)_0{}_{93}(\text{O}^-)_0{}_{08} \cdot 3.27\text{H}_2\text{O}$			
2	0.04	0.8		0.20	Stirred at room temp. 2½ hr	63.35	1.65	7.62		$\text{Th}(\text{O}^-)_1{}_{96}(\text{SO}_4^-)_0{}_{94}(\text{O}^-)_0{}_{07} \cdot 3.44\text{H}_2\text{O}$			
3	0.021	0.68		0.21	Stirred at 50° C overnight	63.38	1.55	7.60		$\text{Th}(\text{O}^-)_1{}_{96}(\text{SO}_4^-)_0{}_{95}(\text{O}^-)_0{}_{07} \cdot 3.20\text{H}_2\text{O}$	0.51	3.11	1.95
4	0.038	2.26		0.31	Nitrate fumed out with H ₂ SO ₄ ; H ₂ O ₂ added; stirred at 70–90° C for 2 hr	64.03	1.57	7.75	21.80	$\text{Th}(\text{O}^-)_2{}_{00}(\text{SO}_4^-)_0{}_{94}(\text{O}^-)_0{}_{08} \cdot 3.24\text{H}_2\text{O}$	0.53	3.12	

*Samples dried in high vacuum for 16 hr.

†Treated in this manner to bring down precipitate. Stirred 2 hr at 67° C.

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Table 7—Analyses of Thorium Peroxide Chloride and Thorium Peroxide Perchlorate in the Absence of Foreign Anions

Sample	Initial [Th ⁴⁺], moles/ liter	Initial [H ₂ O ₂], moles/ liter	Initial [HCl], moles/ liter	Initial [HClO ₄], moles/ liter	Precipitating conditions	ThO ₂ , %	H, %	Peroxide oxygen, %	Cl, %	SO ₄ ²⁻ , %	Formula calculated	O ⁻ /Th ⁴⁺ , wet
1	0.070	0.80	0.4		Stirred at room temp. 2 hr, washed twice	75.85	1.35	12.27			Th(O ⁻) _{2.87} (Cl ⁻) _{0.70} (O ²⁻) _{0.30} · 2.35H ₂ O	
2	0.20	1.1	1.0		H ₂ O ₂ added slowly, stirred 3 hr at room temp., washed twice only because of peptization	75.92	1.26	14.38	5.95		Th(O ⁻) _{3.14} (Cl ⁻) _{0.57} (O ²⁻) _{0.15} · 2.20H ₂ O	
2*								13.71			Th(O ⁻) _{2.90}	
3	0.187	3.3	1.0		Stirred overnight at room temp., washed 4 times	76.35	1.29	14.50	6.87	0.33	Th(O ⁻) _{3.14} (Cl ⁻) _{0.87} (SO ₄ ²⁻) _{0.01} (O ²⁻) _{0.08} · 2.24H ₂ O	3.38
4	0.20	1.1		1.0	H ₂ O ₂ added slowly, stirred at room temp. 3 hr, washed 4 times	65.90	1.39	12.87	4.92		Th(O ⁻) _{3.23} (ClO ₄ ⁻) _{0.56} (O ²⁻) _{0.11} · 2.79H ₂ O	

*Reanalyzed for peroxide oxygen after standing for 1 week

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Table 8—Thorium Peroxide Solids Reported in the Literature

Author	Conditions of precipitation and analysis	Composition from analyses reported
Boisbaudran Chem. News, 51: 148 (1885) Compt. rend., 100: 605 (1885)	Th salt + H_2O_2 + NH_3 , wet	$\text{Th}(\text{O}^-)_{3.48; 3.65; 3.71; 3.54}$ Average = 3.60
Cleve Bull. soc. chim. France, (2) 43: 53 (1885) Ofvers. K. Vet.- Akad. Förh, 3-14 (1885)	$\text{Th}(\text{SO}_4)_2$ + H_2O_2 , wet $\text{Th}(\text{SO}_4)_2$ + H_2O_2 + NH_3 , wet $\text{Th}(\text{SO}_4)_2$ + H_2O_2 + NH_3 , dry	$\text{Th}(\text{O}^-)_{2.82}(\text{SO}_4^{--})_{0.44}(\text{O}^{--})_{0.15} \cdot x\text{H}_2\text{O}$ $\text{Th}(\text{O}^-)_{2.92}(\text{SO}_4^{--})_0(\text{O}^{--})_{0.54} \cdot x\text{H}_2\text{O}$ $\text{Th}(\text{O}^-)_{2.56}(\text{SO}_4^{--})_0(\text{O}^{--})_{0.72} \cdot x\text{H}_2\text{O}$
Pissarjewsky Z. anorg. Chem., 25: 378 (1900) Z. anorg. Chem., 31: 359 (1902)	$\text{Th}(\text{SO}_4)_2$ + H_2O_2 + NH_3 , wet Same sample dried 4 days Same sample stored wet 4 days $\text{Th}(\text{NO}_3)_4$ + H_2O_2 , wet	$\text{Th}(\text{O}^-)_{3.0}$ $\text{Th}(\text{O}^-)_{2.2}$ $\text{Th}(\text{O}^-)_{2.0}$ $\text{Th}(\text{O}^-)_{3.3; 3.0}$
Schwarz and Giese Z. anorg. u. allgem. Chem., 176: 209-232 (1928)	Th^{+4} + H_2O_2 + NH_3 Neutral nitrate solution Acid sulfate solution	"Confirms Th_2O_7 of older authors" $\text{Th}(\text{O}^-)_{2.94}(\text{NH}_3)_{0.33}$ $\text{Th}(\text{O}^-)_{2.80}(\text{NH}_3)_{0.00}$
Wyrouboff and Verneuil Bull. soc. chim. France, (3) 19: 219 (1898)	Not given	$\text{Th}(\text{O}^-)_{3.00}(\text{NO}_3^-)_{1.00}$
Calzolari Gazz. chim. ital., 42 (2): 21 (1912)	4-5°C; thorium salt + H_2O_2 composition of un- washed precipitate de- termined indirectly from analysis of super- natant solution*	

*Analysis of thorium salt used is as follows:

$\text{NO}_3^-/\text{Th}^{+4} = 4.16$	$\text{Th}(\text{O}^-)_{3.1}(\text{NO}_3^-)_{1.0}(\text{H}^+)_{0.1} \cdot x\text{H}_2\text{O}$
$\text{NO}_3^-/\text{Th}^{+4} = 4.16$	$\text{Th}(\text{O}^-)_{3.3}(\text{NO}_3^-)_{1.0}(\text{H}^+)_{0.3} \cdot x\text{H}_2\text{O}$
$\text{NO}_3^-/\text{Th}^{+4} = 4.16$	$\text{Th}(\text{O}^-)_{3.1}(\text{NO}_3^-)_7$
$\text{NO}_3^-/\text{Th}^{+4} = 4.22$	$\text{Th}(\text{O}^-)_7(\text{NO}_3^-)_{1.0}$
$\text{SO}_4^{--}/\text{Th}^{+4} = 1.998$	$\text{Th}(\text{O}^-)_{2.4}(\text{SO}_4^{--})_{0.45}(\text{O}^{--})_{0.3} \cdot x\text{H}_2\text{O}$
$\text{SO}_4^{--}/\text{Th}^{+4} = 1.998$	$\text{Th}(\text{O}^-)_{2.5}(\text{SO}_4^{--})_{0.48}(\text{O}^{--})_{0.3} \cdot x\text{H}_2\text{O}$
$\text{SO}_4^{--}/\text{Th}^{+4} = 1.996$	$\text{Th}(\text{O}^-)_7(\text{SO}_4^{--})_{0.48}$
$\text{Th}(\text{Cl}^-)_{3.29}(\text{O}^{--})_{0.36}$	$\text{Th}(\text{O}^-)_{3.1}(\text{Cl}^-)_{0.50}(\text{O}^{--})_{0.2} \cdot x\text{H}_2\text{O}$
$\text{Th}(\text{Cl}^-)_{3.29}(\text{O}^{--})_{0.36}$	$\text{Th}(\text{O}^-)_{3.4}(\text{Cl}^-)_{0.51}(\text{O}^{--})_{0.1} \cdot x\text{H}_2\text{O}$

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Paper 7.3

A STUDY OF THORIUM PEROXIDE SULFATE

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[Editor's Note: This paper was a contribution from the University of California, Berkeley, and is based on Report CC-3638.]

ABSTRACT

Thorium peroxide was precipitated from thorium nitrate solutions containing varying amounts of sulfate ion and of hydrogen ion. The washed solids were analyzed both wet and dry. Analyses were made for thorium, peroxide oxygen, sulfate, nitrate, and water contents. X-ray powder photographs of the dried samples by W. H. Zachariasen showed the presence of only two phases. When precipitated from high sulfuric acid, the solid phase was isomorphous with $\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$. More weakly acid solutions whose sulfate content was varied over wide limits $[\text{SO}_4^{--}/\text{Th}(\text{IV})]$ (in solution before precipitation) = 0.005 to 67.0] yielded a solid, isomorphous with thorium peroxide nitrate and containing 3.0 to 3.8 peroxide oxygen atoms for each thorium atom. The sulfate content of this latter phase varied continuously between the limits $\text{SO}_4^{--}/\text{Th}(\text{IV}) = 0.34$ to 0.01 with nitrate ion present when the sulfate content was very low. This continuous variation in composition is in agreement with the previously proposed structure of this phase.

In a previous study of the peroxides of thorium¹ it was found that the insoluble peroxide formed in 1N H_2SO_4 corresponded closely to the empirical formula $\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$. Work done by Koshland, Dam, Kroner, Moore, and Spector,² using 0.1N H_2SO_4 , showed the formation of a compound which contained 3 peroxide oxygen atoms for each thorium atom. A compound similar to that prepared by Koshland and coworkers has been reported in the literature.³⁻⁵

The available data indicated therefore that the concentration of sulfuric acid determines which of the two types of compound is to be formed. In high concentrations of sulfuric acid, $\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$ is formed, whereas at lower concentrations a quite different compound is formed containing considerably more peroxide oxygen. These data, however, did not show the effect of variation in the relative proportions of sulfate and hydrogen ions, so a series of experiments was performed in which the sulfate and hydrogen ion contents were varied individually and over wide limits.

In these experiments an acid solution of thorium nitrate containing a known added quantity of sulfate was treated with hydrogen peroxide, and the mixture was stirred overnight. The precipitated peroxide was then washed with water and divided into two portions. One portion was dried in a vacuum desiccator for approximately 2 days and analyzed completely by microcombustion methods, whereas the second portion was analyzed for peroxide oxygen and thorium immediately after washing and without any drying treatment. The methods of analyses used are described in a previous paper.¹

In most cases hydrogen ion in the precipitation solution was supplied by sulfuric acid, but, where the sulfate content used did not permit the addition of this amount of sulfuric acid, the deficit was made up with nitric acid. In order to vary the sulfate content, ammonium sulfate was added. The experimental results are summarized in Table 1. They are presented in two series: Series A, in which the stoichiometric amount of sulfate in the solution is kept constant while the amount of hydrogen ion is varied, and Series B, in which the sulfate content is changed with no variation in the hydrogen ion content (there was, however, a change in the hydrogen ion concentration since $\text{H}^+ + \text{SO}_4^{--} = \text{HSO}_4^-$).

In Series A we seem to have a transition from one of the two types of peroxide to the other. The peroxide formed from the solution with the highest concentration of hydrogen ion (sample 155, formed from 2.0N H^+) was quite different in appearance from the other two samples formed at lower acidities. It was flocculent rather than gelatinous and was far more dense. It had the general appearance of $\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$ while the peroxides formed at lower acidities resembled thorium peroxide nitrate. From Table 1 it will be seen that the composition of sample 155 is nearly that of samples of $\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$ previously prepared and analyzed. If a correction is applied for the loss of peroxide oxygen on drying, the composition may be represented by the formula $\text{Th}(\text{O}^-)_{1.99}(\text{SO}_4^{--})_{0.86}(\text{O}^{--})_{0.15} \cdot 3.05\text{H}_2\text{O}$, which is to be compared with $\text{Th}(\text{O}^-)_{1.99}(\text{SO}_4^{--})_{0.94}(\text{O}^{--})_{0.07} \cdot 3.44\text{H}_2\text{O}$ (reference 1). The sample obtained in the experiment reported here was formed with only an equivalent quantity of sulfate present in the solution, whereas all other

samples of $\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$ were precipitated in the presence of a large excess of sulfuric acid. This difference is probably responsible for the comparatively low sulfate content in this case. The loss of peroxide oxygen by sample 155, upon drying, is in sharp contrast to the stability exhibited by all samples of $\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$ prepared previously and perhaps indicates an important difference.

W. H. Zachariasen subjected the dried peroxides to x-ray analysis⁶ and found only two phases represented. In sample 155, he found only phase I, i.e., the phase corresponding to $\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$, whereas in all the other samples only phase II, corresponding to thorium peroxide nitrate, was detected. Thus sample 155 is in fact isomorphous with $\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$, whereas the rest of the peroxides are isomorphous with thorium peroxide nitrate. Any other phases which may be present in the dry material are evidently insufficiently crystalline or present in too small an amount to be detected by x-rays.

For phase II the variations in hydrogen and sulfate ion concentrations have little, if any, effect on the peroxide oxygen content of the precipitates. With few exceptions the undried material contains approximately 3 peroxide oxygen atoms for each thorium atom. The exceptions occur at very low sulfate contents (omitting sample 151, which was digested at 85°C). These cases are not surprising, however, since earlier work¹ has shown that thorium peroxide precipitated from nitric acid contains up to 3.5 peroxide oxygen atoms per thorium atom and in these cases nitrate is present in great excess over sulfate.

These observations are in agreement with the structure that has been proposed for phase II in a previous report.¹ On the basis of x-ray powder diffraction patterns, Zachariasen has suggested that in this phase the thorium atoms are arranged with hexagonal symmetry in two dimensional sheets. From this and other evidence, it has been postulated that these sheets consisted of only thorium and peroxide atoms in such a ratio that the layers had a net positive charge and were therefore neutralized by various anions such as nitrate, sulfate, hydroxide, etc. In no case, including the work reported here, has the peroxide content of an undried precipitate with phase II structure been less than 3 peroxide oxygen atoms for each thorium atom, and so it has been concluded that this is probably the ratio in the sheets of thorium and peroxide. The presence of more peroxide in certain cases is interpreted as being due to OOH (or OO^-) between the layers of thorium and peroxide oxygen atoms.

Sample 125 in Table 1 duplicates an experiment reported by Koshland and coworkers² in which thorium peroxide formed from solutions containing a deficiency of hydrogen peroxide was found to contain 3 peroxide oxygen atoms per thorium atom. Under such precipitation

conditions it might be expected that only the layers of thorium atoms would contain peroxide oxygen since there was not enough peroxide to go around. This would support the suggestion that the layers contained 3 peroxide oxygen atoms for each thorium atom.

The composition of the dry solids in Series B is of interest because of the trend that is observed in sulfate content. As the sulfate content of the solution increases continuously, the sulfate content of the solid likewise changes continuously, first increasing, then decreasing, and finally increasing. The fact that the sulfate content changes continuously although only one phase was found to be present is in agreement with the structure for phase II which was discussed above. As would be concluded from that structure, sulfate, nitrate, hydroxide, perhydroxide, and other anions seem to be loosely bound in the compound, and it is apparently relatively easy to replace one type of anion with another. The relative proportions of the various anions can vary continuously, and the amount of any one ion in the compound can therefore vary continuously between limits set by the total amount of "loosely bound" anion.

The peroxide content of a dried solid indicates only the stability of the solid under the drying conditions that were used. From Table 1 it will be observed that the stability in Series B is inversely proportional to the sulfate content—the more sulfate, the less peroxide. This is in contrast to $\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}$, which is very stable but has a higher sulfate content.

Inspection of Series B in Table 1 will show that the highest sulfate content was $0.34 \text{ SO}_4^{--}/\text{Th}^{+4}$ and that hydroxide ion is therefore present in all the samples. The variation in the sulfate contents observed in Series B can be regarded as a variation in the ratio of sulfate to hydroxide ions in the compound. In the first few samples (130, 128, 127, and 124), however, perhydroxide and nitrate ions are also taken up because only a very small amount of sulfate was available in the solution.

The exchange of sulfate and hydroxide ions can be represented by the equation $(\text{Th}_{\text{peroxide solid}}) \cdot \text{SO}_4 + 2\text{OH}^- = (\text{Th}_{\text{peroxide solid}}) \cdot 2\text{OH} + \text{SO}_4^{--}$, and accordingly the sulfate content of the solids in Series B, Table 1, should be determined by the ratio $(\text{SO}_4^{--})/(\text{OH}^-)^2$ in the precipitation solution. By using the ion product for H_2O and the constant for the sulfate-bisulfate equilibrium, this is shown to be proportional to the product $(\text{H}^+)(\text{HSO}_4^-)$. The peroxide concentration was kept constant throughout these experiments, and perhydroxide displaces sulfate by the same equation; therefore product $(\text{H}^+)(\text{HSO}_4^-)$ was calculated for all cases both before and after precipitation of thorium peroxide. These two cases differ because hydrogen ion is released and sulfate

is absorbed when the compound is formed. A value of 0.012 was used for the bisulfate constant, and no effort was made to correct for the hydrolysis of thorium. It was assumed, in order to calculate the conditions after precipitation, that thorium peroxide was completely precipitated. In view of the high peroxide concentration this is probably not greatly in error. The results of these calculations, together with the sulfate-to-thorium ratio of the dried solids, are given in Table 2.

The first point to be noted is that before precipitation the product $(\text{H}^+)(\text{HSO}_4^-)$ for sample 155 is the largest of any on the table and that likewise the solid contains considerably more sulfate than any other precipitate. After precipitation this is not the case, since the value of the product $(\text{H}^+)(\text{HSO}_4^-)$ is lower than, for example, the values which apply to sample 156 both before and after precipitation. Nevertheless, sample 156 contains considerably less sulfate than sample 155. The possibility exists that most of the thorium precipitated as phase I $[\text{Th}(\text{OO})\text{SO}_4 \cdot 3\text{H}_2\text{O}]$ type structure until the product $(\text{H}^+)(\text{HSO}_4^-)$ dropped to a certain critical value lying between 9.6×10^{-2} and 1.5×10^{-2} , after which phase II (peroxide nitrate type structure) separated. It would be expected that the admixture of phase II would explain the low sulfate content $[\text{SO}_4^{--}/\text{Th}(\text{IV}) = 0.86 \text{ instead of } 0.94]$.¹ However, if the material consisted of 13 per cent $\text{Th}(\text{O}^-)_3(\text{SO}_4^{--})_{0.3}(\text{OH}^-)_{0.4}$ and 87 per cent $\text{Th}(\text{O}^-)_{1.99}(\text{SO}_4^{--})_{0.94}(\text{OH}^-)_{0.13}$, it would contain on the average 0.86 sulfate ion per thorium atom, but it would contain 2.12 peroxide oxygen atoms per thorium atom, which is 6 per cent higher than what was actually found. It seems possible therefore that the precipitation of thorium stopped when the critical value of the product was reached, leaving a certain amount of thorium unprecipitated. The high concentration of hydrogen peroxide present would make incomplete precipitation unlikely except that the acidity of the solution was higher than in any other experiment in Table 1.

With the exception of samples 150, 153, and 154, the trend of sulfate content of the other solids is consistent with the product $(\text{H}^+)(\text{HSO}_4^-)$ calculated for the composition before precipitation but not the values calculated for the solutions after precipitation. Thus the product $(\text{H}^+)(\text{HSO}_4^-)$ before precipitation rises to a maximum at sample 129, which also represents a maximum in the sulfate content of the solids. Both the product $(\text{H}^+)(\text{HSO}_4^-)$ and the sulfate content of the solids fall off together until sample 149, after which the relation fails since the sulfate content of the solid rises while the product continues to decrease. The product $(\text{H}^+)(\text{HSO}_4^-)$ for the solution after precipitation reaches a maximum at a later point and so does not fit the facts accurately. With regard to the last region which does not agree with

the thermodynamic predictions, data reported by Britton⁷ are applicable. He reports potentiometric titrations of thorium with hydroxide which show the first visible precipitation of thorium hydroxide to occur at 0.007M H^+ . Table 2 will show that the pH is high enough in the case of samples 154, 153, and 150 that there may have been some colloidal hydroxide in the solution before precipitation. He concludes moreover from the shape of the titration curve that the first hydroxide precipitate from thorium sulfate solutions contains greater than 0.3 sulfates per thorium. It seems possible therefore that there was some entrainment of sulfate by this mechanism and that there is sulfate present in the solid peroxides although at equilibrium there ought to be little or none. It has been found in unpublished work that, even after 119 days of dialysis with water, 30 per cent of the sulfate initially present remains in this type of thorium peroxide sulfate, so it is quite unlikely that stirring overnight was sufficient to bring the solid into equilibrium with the solution. The fact that no nitrogen was found in these samples shows that there was no adsorption of the cation NH_4^+ .

Attention should be called to sample 151 in Table 1. This sample differs from the other samples in that it was digested at 85°C for 4 hr. As a result it contains more peroxide oxygen than other samples prepared under somewhat comparable conditions. This behavior is in agreement with that reported for plutonium peroxide sulfates precipitated from heated nitrate solutions.⁸

Table 1 — Analyses of Thorium Peroxide Sulfates*

Sample	Initial [Th ⁴⁺], moles/ liter	Initial [H ₂ O ₂], moles/ liter	Initial Σ [H ⁺], moles/ liter†	Initial Σ[SO ₄ ²⁻]/ [Th ⁴⁺]†	Dry analysis					Wet analysis		Phase from x-ray analysis	
					ThO ₂ , %	H, %	Peroxide oxygen, %	NO ₂ , %	SO ₄ , %	Peroxide oxygen			
										Th			
Series A‡													
129	0.056	3.27	0.114	1.0	73.02	1.34	8.42	0.0	8.93	3.05	Th(O ⁻) _{1 81} (NO ₂ ⁻) _{0 00} (SO ₄ ²⁻) _{0 34} (O ⁻) _{0 71} ·2.43H ₂ O	II	
156	0.055	3.2	0.51	1.0	74.37	1.34	12.70	0.0	9.21	3.10	Th(O ⁻) _{2 82} (NO ₂ ⁻) _{0 00} (SO ₄ ²⁻) _{0 34} (O ⁻) _{0 25} ·2.38H ₂ O	II	
155	0.049	2.9	2.02	1.0	65.34	1.51	6.92	0.0	20.49	1.99	Th(O ⁻) _{1 74} (NO ₂ ⁻) _{0 00} (SO ₄ ²⁻) _{0 86} (O ⁻) _{0 27} ·3.05H ₂ O	I	
Series B‡													
130	0.057	3.3	0.070	0.005	72.36	1.28	14.88	7.75	0.27	3.40	Th(O ⁻) _{3 89} (NO ₂ ⁻) _{0 46} (SO ₄ ²⁻) _{0 01} (O ⁻) _{0 06} ·2.34H ₂ O	II	
128	0.057	3.29	0.067	0.053	73.19	1.36	14.48	5.71	0.48	3.78	Th(O ⁻) _{3 23} (NO ₂ ⁻) _{0 33} (SO ₄ ²⁻) _{0 02} (O ⁻) _{0 20} ·2.46H ₂ O	II	
127	0.057	3.29	0.067	0.3	74.07	1.35	14.20	0.0	5.27	3.49	Th(O ⁻) _{3 14} (NO ₂ ⁻) _{0 00} (SO ₄ ²⁻) _{0 20} (O ⁻) _{0 23} ·2.41H ₂ O	II	
126	0.057	3.29	0.079	0.7	76.51	1.21	9.78	0.0	5.33	3.08	Th(O ⁻) _{2 11} (NO ₂ ⁻) _{0 00} (SO ₄ ²⁻) _{0 19} (O ⁻) _{0 76} ·2.09H ₂ O	II	
124	0.057	3.29	0.079	0.7	76.82	1.36	9.78	0.97	4.58	3.08	Th(O ⁻) _{2 10} (NO ₂ ⁻) _{0 06} (SO ₄ ²⁻) _{0 16} (O ⁻) _{0 77} ·2.34H ₂ O	II	
125§ (defi- cient in H ₂ O ₂)	0.084	0.097	0.116	0.7	74.02	1.23	9.04	0.44	9.14	3.08	Th(O ⁻) _{2 02} (NO ₂ ⁻) _{0 02} (SO ₄ ²⁻) _{0 34} (O ⁻) _{0 84} ·2.20H ₂ O		
129	0.056	3.27	0.114	1.0	73.02	1.34	8.42	0.0	8.93	3.05	Th(O ⁻) _{1 81} (NO ₂ ⁻) _{0 00} (SO ₄ ²⁻) _{0 34} (O ⁻) _{0 71} ·2.43H ₂ O	II	
143	0.056	3.2	0.066	1.5	74.49	1.39	8.68	0.0	7.76	3.04	Th(O ⁻) _{1 82} (NO ₂ ⁻) _{0 00} (SO ₄ ²⁻) _{0 29} (O ⁻) _{0 75} ·2.47H ₂ O	II	
144	0.055	3.2	0.066	2.0	76.44	1.29	8.74	0.0	6.23	2.96	Th(O ⁻) _{1 89} (NO ₂ ⁻) _{0 00} (SO ₄ ²⁻) _{0 23} (O ⁻) _{0 83} ·2.22H ₂ O		
145	0.054	3.2	0.066	3.0	76.98	1.34	9.40	0.0	4.80	3.08	Th(O ⁻) _{2 02} (NO ₂ ⁻) _{0 00} (SO ₄ ²⁻) _{0 17} (O ⁻) _{0 82} ·2.30H ₂ O	II	
149	0.051	3.1	0.062	4.9	79.58	1.39	12.22	0.0	2.25	3.02	Th(O ⁻) _{2 84} (NO ₂ ⁻) _{0 00} (SO ₄ ²⁻) _{0 06} (O ⁻) _{0 82} ·2.31H ₂ O	II	
150	0.052	3.1	0.064	9.1	76.77	1.36	12.92	0.0	3.45	3.17	Th(O ⁻) _{2 78} (NO ₂ ⁻) _{0 00} (SO ₄ ²⁻) _{0 12} (O ⁻) _{0 49} ·2.34H ₂ O	II	
151	0.051	3.0	0.064	19.9				0.0	5.07	3.61	Th(O ⁻) _{2 84} (NO ₂ ⁻) _{0 00} (SO ₄ ²⁻) _{0 18} (O ⁻) _{0 40} ·2.26H ₂ O	II	
153	0.049	2.8	0.064	41.1	75.86	1.42	12.08	0.0	6.27	3.05	Th(O ⁻) _{2 83} (NO ₂ ⁻) _{0 00} (SO ₄ ²⁻) _{0 23} (O ⁻) _{0 45} ·2.48H ₂ O	II	
154	0.044	2.6	0.064	67.0	74.99	1.36	12.56	0.0	7.86	3.12	Th(O ⁻) _{2 76} (NO ₂ ⁻) _{0 00} (SO ₄ ²⁻) _{0 29} (O ⁻) _{0 33} ·2.40H ₂ O	II	

*Thorium nitrate was used as a source of thorium.

†The summation symbols are used to indicate stoichiometric concentration, not the true concentration of the ionic species indicated

‡Precipitation conditions for all samples except sample 151, Series B, consisted in stirring at room temperature overnight. Sample 151, Series B, was heated at 85°C for 4 hr.

§Considered separately from the rest of the series.

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Table 2 — H^+ , HSO_4^- , and SO_4^{--} Concentrations in Solution Before and After Precipitation of Thorium Peroxide*

Sample	Before precipitation				After precipitation†				SO ₄ ²⁻ /Th in dried peroxide
	[H ⁺]	[SO ₄ ²⁻]	[HSO ₄ ⁻]	[H ⁺][HSO ₄ ⁻]	[H ⁺]	[SO ₄ ²⁻]	[HSO ₄ ⁻]	[H ⁺][HSO ₄ ⁻]	
Series A									
129	0.068	0.0085	0.048	3.3 × 10 ⁻³	0.223	0.002	0.044	9.8 × 10 ⁻³	0.34
156	0.456	0.0014	0.054	2.4 × 10 ⁻²	0.637	0.001	0.035	2.3 × 10 ⁻²	0.34
155	1.97	0.00030	0.049	9.6 × 10 ⁻²	2.13	0.000	0.007	1.5 × 10 ⁻²	0.86
Series B									
130	0.070	0.00004	0.00024	1.7 × 10 ⁻⁵	0.264				0.01
128	0.064	0.00048	0.0025	1.6 × 10 ⁻⁴	0.280	0.00008		5.3 × 10 ⁻⁴	0.02
127	0.053	0.0032	0.0139	7.4 × 10 ⁻⁴	0.260	0.00025	0.0055	1.4 × 10 ⁻³	0.20
126	0.046	0.0083	0.0316	1.5 × 10 ⁻³	0.228	0.002	0.028	6.4 × 10 ⁻³	0.19
124	0.046	0.0083	0.0316	1.5 × 10 ⁻³	0.226	0.002	0.029	6.6 × 10 ⁻³	0.16
129	0.068	0.0085	0.048	3.3 × 10 ⁻³	0.223	0.002	0.044	9.8 × 10 ⁻³	0.34
143	0.017	0.035	0.049	8.3 × 10 ⁻⁴	0.158	0.006	0.078	1.2 × 10 ⁻²	0.29
144	0.0119	0.056	0.054	6.4 × 10 ⁻⁴	0.128	0.009	0.101	1.3 × 10 ⁻²	0.23
145	0.0069	0.103	0.059	4.1 × 10 ⁻⁴	0.089	0.019	0.143	1.3 × 10 ⁻²	0.17
149	0.0037	0.192	0.058	2.2 × 10 ⁻⁴	0.033	0.067	0.183	6.0 × 10 ⁻³	0.08
150	0.0018	0.411	0.062	1.1 × 10 ⁻⁴	0.010	0.254	0.219	2.2 × 10 ⁻³	0.12
153	0.00039	1.97	0.064	2.5 × 10 ⁻⁵	0.001	1.82	0.212	2.1 × 10 ⁻⁴	0.23
154	0.00027	2.88	0.064	1.8 × 10 ⁻⁵	0.0008	2.75	0.201	1.6 × 10 ⁻⁴	0.29

*All concentrations in moles per liter.

†Complete precipitation of the solid was assumed.

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Paper 7.4

NOTE ON ELECTROLYSIS OF THORIUM CHLORIDE FROM FUSED SALTS

By E. D. Eastman, A. E. Stickland, and B. J. Fontana

[Editor's Note: This paper was a contribution of the University of California, Berkeley, and is based on Reports CC-1740 and CC-3635.]

A tungsten rod served as cathode. This was dipped into a porous alundum cup containing a potassium chloride-sodium chloride equimolar mixture to which was added approximately 10 mole % thorium chloride (see Report CC-1222 by A. E. Stickland, Berkeley, Dec. 31, 1943, for method of purification of thorium chloride). An impure thorium strip served as the anode. It was immersed in a potassium chloride-sodium chloride equimolar mixture outside the porous alundum cup. The outer container was a quartz tube 1 in. in diameter.

The electrolysis was carried out at 665°C in a helium atmosphere. A current of 0.4 amp was passed for 40 min at about 1.7 volts. The voltage remained essentially constant throughout the electrolysis. The cathode deposit was a mass of small crystals having a metallic luster. The deposit was freed from the fused salt by washing with water and was dried in vacuo. The weight of the cathode deposit was approximately 0.2 g, and analysis revealed the following composition: 87 per cent Th (as free metal), 13 per cent ThO_2 . The oxide may have resulted from the water washing. The current efficiency was approximately 33 per cent.

Paper 7.5

NOTE ON METHODS OF PURIFICATION AND ANALYSIS
OF ANHYDROUS THORIUM CHLORIDE

By E. D. Eastman and A. E. Stickland

[Editor's Note: This paper was a contribution of the University of California, Berkeley, and is based on Reports CC-1222 and CC-3636. Prepared for publication by C. D. Thurmond, following demise of the senior author.]

Water, ammonium chloride, and hydrochloric acid are removed from impure thorium tetrachloride when vacuum heated to 200°C. On being transferred to a quartz container and reheated in a vacuum to temperatures up to 1000°C, the thorium chloride sublimes to the cooler portions of the container, leaving a residue which generally consists of thorium oxide. Some oxychloride may remain.

A rapid determination of oxide and oxychloride impurities in thorium tetrachloride may be made by extracting the tetrahalide with absolute ethyl alcohol. Attempts to isolate the pure tetrachloride from the alcohol failed since the compound $\text{ThCl}_4 \cdot 4\text{C}_2\text{H}_5\text{OH}$ was formed and charred a great deal when heated slowly up to 250°C under a partial vacuum.

Paper 7.6

A PHYSICAL STUDY OF THE THORIUM-HYDROGEN SYSTEM

By R. W. Nottorf, A. S. Wilson, R. E. Rundle, A. S. Newton,
and J. E. Powell

[Editor's Note: This paper was a contribution of Iowa State College and is based on Report CC-2722.]

ABSTRACT

The thorium-hydrogen system has been studied by vapor pressure and x-ray methods. Both reveal two hydrides of thorium, one of composition ThH_2 and one of $\text{ThH}_{3.75}$ or 4. (The latter appears identical with the reported ThH_3 .)

The dissociation pressure of the two hydrides has been determined as a function of temperature and composition, and ΔH (formation) has been found for the hydrides.

The lower hydride (ThH_2) is isomorphous or pseudoisomorphous with ThC_2 , ZrH_2 , and ZrC_2 , with a pseudotetragonal body-centered unit containing two metal atoms. The higher hydride is cubic. The structure has been reported previously.

1. INTRODUCTION

The reaction of thorium metal with hydrogen to form thorium hydride was first reported in 1891 by Winkler,¹ who claimed to have produced ThH_2 from thorium metal containing ThO_2 and some magnesium. Matignon and Delépine² claimed the production of ThH_4 and $\text{ThH}_{3.8}$ from metal containing 26 per cent ThO_2 , while Sieverts and Roell³ and Katz and Davidson⁴ were unable to get hydrogen contents of more than approximately $\text{ThH}_{3.1}$ based on the weight of free thorium in the sample as determined by chemical analysis. The latter workers^{3,4} made extensive dissociation-pressure-composition-tem-

perature studies on the thorium-hydrogen system and plotted hydrogen content of the solid as a function of temperature at constant hydrogen pressure. They found a rapidly decreasing hydrogen content with increasing temperature in the 100 to 200°C range, then a slower decrease, and a sharp drop in the hydrogen content between 800 and 1000°C. They also plotted isotherms (dissociation pressure plotted as a function of hydrogen content of the solid at constant temperature) and obtained widely varying results, depending on whether hydrogen was added to, or removed from, the solid. These workers favored the concept that the thorium-hydrogen system was of the solid-solution type and similar to the palladium-hydrogen system.

The first positive evidence that the association of hydrogen with thorium metal involves compound formation rather than the formation of a solid solution was presented by Zachariasen.⁵ A sample of composition ThH_3 proved to have a unique cubic structure not related to that of thorium metal. The structure excludes the possibility that this hydride is an interstitial compound or a solid solution of hydrogen in metal.

2. PHYSICOCHEMICAL STUDIES OF THORIUM HYDRIDE

2.1 Decomposition-pressure - Composition - Temperature Studies.

Equilibrium-pressure studies of thorium hydride have been made as a function of temperature and composition. The equilibrium pressure was approached from both sides by studying the pressure developed (a) when thorium hydride was decomposed into a vacuum and (b) when hydrogen at a higher pressure was added to the system and the pressure was reduced to the equilibrium pressure by the reaction of the lower hydride or metal with the excess hydrogen added.

The apparatus in which the equilibrium-pressure studies were made is shown diagrammatically in Fig. 1. The sample bulb was of quartz with a quartz-to-pyrex seal in its neck. The bulb and its manometer system contained as small a volume as possible to permit a rapid approach to equilibrium. The actual volume was 16 to 22 ml, depending on the position of the mercury in the manometer. This smaller system was connected to a larger glass manifold to which were attached a manometer, an Ace compact-type McLeod gauge, a gas-storage bulb, a uranium hydride bulb for generating hydrogen, and a vacuum connection through a mercury pump to a Cenco Pressovac pump. The volumes of the various parts of the system were determined by filling them with a dry inert gas at a known pressure and temperature, evacuating through the Pressovac pump, collecting the gas at the exit from the pump, and measuring the volume by water

displacement from a Mariotte bottle. The volume of water displaced is a measure of the volume of the system if allowance is made for temperature and pressure differences, hydrostatic head, and water-vapor pressure.

The sample of thorium hydride in the quartz bulb was heated by a resistance furnace, the temperature of which could be controlled to an accuracy of $\pm 2^\circ\text{C}$ by the temperature-control apparatus described in a report by Newton, Nottorf, and Powell.⁶

Two techniques were used to obtain the equilibrium pressure as a function of composition at various temperatures. The first, yielding the results plotted in Fig. 2, was to assemble the apparatus with a known weight of clean thorium metal in the sample bulb and to convert the sample to its hydride of highest obtainable hydrogen content. This was done by filling the system with a known amount of hydrogen, calculated from the volume, pressure, and temperature of the system, and heating the sample to start the reaction. Usually reaction began at 300 to 350°C, but most samples were heated to 450 to 500°C and then allowed to cool slowly by shutting off the power to the furnace. The system was refilled with measured amounts of hydrogen, if necessary, to maintain an excess of hydrogen pressure as the system cooled. The hydrogen content of the solid phase was taken as the total hydrogen content of the system less the unabsorbed hydrogen in the gas phase. At this highest hydrogen content the sample was isolated from the main volume of the system by closing the connecting stopcock, and the sample was heated. The "equilibrium pressure" at this composition was then measured at various temperatures, holding each temperature constant to $\pm 2^\circ\text{C}$. At high temperatures the dissociation pressure reached the maximum pressure measurable, so the composition of the sample was changed by withdrawing an appropriate amount of hydrogen from the system through a Pressovac pump and measuring it by water displacement from a Mariotte bottle. The system was then cooled to room temperature, and a new series of readings was made at the new composition, again with progressively increasing temperatures. Thus all pressure values in Fig. 2 were obtained by dissociation of preformed hydride.

When necessary to measure low pressures, 0 to 5 mm, the McLeod gauge was used. In this case the gas occupied the necessarily larger volume, but the connecting stopcock was again closed as soon as the pressure could be measured on the small manometer. When the dissociation pressure was large, the hydrogen in the gas phase was subtracted from the total content of the system in order to find the composition of the solid phase.

The pressure values plotted in Fig. 2 are constant values reached after standing at the given temperature, or they are ranges through which the pressure fluctuated when the temperature was held constant. In most cases in the $\text{ThH}_2\text{-ThH}_x\text{-H}_2$ system ($x = 3.75$ or 4), nearly constant readings were obtained after 1 to 5 hr heating at a constant temperature. In the $\text{Th-ThH}_2\text{-H}_2$ system, constant pressures were obtained in from 5 to 10 min.

The isotherms in Fig. 3 were obtained in a different way. In this case the temperature was held constant throughout the experiment. Powdered metal, obtained by pumping hydrogen from a thorium hydride sample at temperatures as high as 950°C , was used as a starting material. Hydrogen was admitted in appropriate amounts to establish the desired composition, and after each addition the system was allowed to stand until the pressure became static. These additions were continued until hydride formation was complete. Then by a similar process of isothermal decomposition of the hydride the composition was taken back to powdered metal. Of course, since the two different hydrides had to be studied in different temperature ranges, it was necessary to change the temperature when going from the Th-ThH_2 range to the $\text{ThH}_2\text{-ThH}_x$ range.

Constant pressure values were reached at the end of 5 to 10 min in the Th-ThH_2 system at 700°C , and pressures obtained on formation of the lower hydride equaled those obtained by decomposition. With the $\text{ThH}_2\text{-ThH}_x$ system at 300°C , the approach to constant pressure was much slower; a nearly constant reading was reached only after the system had stood from 30 min to 24 hr. It can be seen from Fig. 3 that even after these times the formation pressures of the higher hydride were much greater than the decomposition pressures.

2.2 Thermodynamic Properties of the Thorium Hydrides. The dissociation-pressure curves of Fig. 2 can be analyzed to give the heats of reaction for each of the steps in hydride formation. The graphs of $\log P$ vs. $1/T$ are shown in Fig. 4 for the composition ratios 0.5 H/Th and 1.5 H/Th ; they are shown in Fig. 5 for the compositions 2.4 H/Th and 3.2 H/Th . The slope,

$$\frac{d \log P}{d(1/T)}$$

gives $\Delta H/2.303 R$, where H is the heat of formation per mole of hydrogen added and R is the molar gas constant. In this manner the heats of reaction were calculated for the reactions shown in Table 1.

The dissociation pressures of the two compounds are given by the following equations, calculated for the center of the flat regions of the isotherms:

Th-ThH₂ system

$$\log P \text{ (mm)} = -\frac{7700}{T} + 9.54$$

ThH₂-ThH_x system ($x = 3.75$ or 4)

$$\log P \text{ (mm)} = -\frac{4220}{T} + 9.50$$

It is to be noted from the calculations of ΔH that the differential heat evolved upon hydrogen absorption is greater at an H/Th ratio of 1.5 than at 0.5 and that it is greater at an H/Th ratio of 3.2 than at 2.4. Figures 4 and 5 illustrate this difference in ΔH graphically.

2.3 Effect of Impurities on Thorium Hydride Formation. The maximum amount of hydrogen which a thorium sample will absorb varies with the sample and its method of preparation. Thorium metal used in this experiment was all produced by the bomb reduction of ThF₄ by calcium, using ZnCl₂ as a booster.⁷ Some of the material was recast in BeO crucibles, in which case it was essentially free of Zn but contained combined thorium, as analyzed by hydrogen evolution upon solution in HCl. The combined thorium was probably oxide. To avoid oxide solubility in thorium, the clean metal "biscuit" from the reduction was heated in a high vacuum at a temperature less than the melting point of thorium to distill out the zinc and leave pure thorium residue. After heating to 1100°C, a spongy thorium with a fibrous structure remained. It contained approximately 0.03 per cent Zn. After heating to 1600°C, the metal was still somewhat spongy and porous, but its macro appearance was much more solid than fibrous. It still contained a small amount of zinc.

The recast thorium formed a hydride of maximum hydrogen content ThH_{3.19}, the 1100°C biscuit formed ThH_{3.52}, and the 1600°C biscuit formed ThH_{3.82}, all based on total weight of metal sample taken. The continued increase in amount of hydrogen reacting leaves little room for doubt that the higher hydride, with completely pure metal, has a formula ThH_{3.75} or ThH₄ (see Sec. 3.4). In a partially completed pressure isotherm from a cast thorium sample, the pressure values were much less sharp, and the "flat" portions of the curves were narrower, more sloping, and, in general, much more poorly defined. It is probable that the previous investigators have worked with thorium of this type and so did not detect the more subtle characteristics of the purer thorium-hydrogen system.

In this laboratory it was found that thorium samples could be converted to hydride, completely decomposed under a vacuum at 900°C,

and converted completely to hydride again. This is contrary to previous reports^{3,4} which indicate that heating to a high temperature lessens the amount of hydrogen a sample can absorb. Explanation for the other behavior could lie in the impurity of their samples or the possibility that previous investigations had decomposed their samples only to ThH_2 . The total amount of hydrogen which a given sample will absorb when cooled slowly to room temperature in hydrogen does not depend on previous heating to high temperatures, except when the temperatures are high enough to cause reaction of the metal with the walls of the vessel. Powdered thorium reacts immediately with H_2 at room temperature, becoming red hot. At room temperature ThH_2 reacts very slowly with H_2 , but the rate gradually increases, and after a few minutes the sample begins to get warm, which increases the rate rapidly.

3. X-RAY STUDIES OF THORIUM HYDRIDE

3.1 Preparation of Samples for X-ray Study. For x-ray investigation of the Th-H system a series of powder samples of known Th-H compositions was required. Each sample was sealed in a small glass or quartz capillary without having ever come into contact with air. The purest thorium hydride is nearly as pyrophoric as UH_3 , and contact with air places an uncertainty on the composition of the sample even if the sample does not burn outright.

The apparatus in which the samples were prepared is shown diagrammatically in Fig. 6. It was of pyrex glass and consisted essentially of a special reaction bulb attached through a stopcock and ground-glass joint to a vacuum system. The system included a manometer, a connection to a hydrogen supply, and a connection to a mercury pump backed by a Pressovac pump. To the reaction bulb, which was of about 15 ml volume, were attached from 5 to 7 capillary "teats." These were made from 4-mm pyrex tubing by blowing a small, thin-walled bulb in one end and pulling the thin-walled section into a capillary by the use of a small pyrex cane and a medium soft flame. The capillaries were selected to a diameter of 0.2 to 0.3 mm and sealed off at 3 to 4 in. The 4-mm base tubing, cut $\frac{1}{2}$ to $\frac{3}{4}$ in. long, was then sealed to the reaction bulb. A pyrex-wool plug kept the thorium metal and hydride from being shaken or blown from the bulb into the vacuum system. A resistance furnace, whose temperature was controlled by a Variac and measured by a thermocouple, surrounded the bulb and capillary system.

To prepare a series of x-ray samples, a known amount of thorium metal (approximately 7 g) was placed in the bulb, to which leak-free

capillaries had already been sealed. The glass-wool plug was put in place and anchored by indentations in the glass, and the bulb was sealed to the connecting stopcock. The volumes of the entire system and its parts were determined by filling to a known pressure with an inert, dry gas and evacuating, the gas being collected as previously described.

The metal was then heated to 400 to 450°C under a vacuum and shut off from the vacuum system by closing the connecting stopcock. The rest of the system was filled with hydrogen at measured pressure and temperature and in known volume, and this measured hydrogen was allowed to react with the sample. The initial reaction heated the sample to bright red heat, and the incoming hydrogen had to be controlled by the adjustment of the stopcock to keep the pyrex bulb from getting too hot. When the initial violence of the reaction was past, the furnace was turned off, and the sample was slowly cooled while more measured hydrogen was added to the system to keep sufficient pressure to complete the reaction. When the sample had cooled to room temperature, the excess hydrogen in the system was measured and evacuated.

Thorium metal prepared by different methods breaks up with different characteristics when it is converted to hydride. Cast thorium seems to exfoliate much like uranium, except that it throws off fine particles to a distance of several inches. The pure spongy thorium often did not break up by itself but could be partly broken up by shaking the sample vigorously. X-ray samples were taken by closing the stopcock to the bulb, removing it from the vacuum system, and shaking fine powdered hydride into the capillaries until the tip of one held a sample to a depth of 5 mm or so. The rest of the hydride was shaken back into the bulb, and the sample capillary was sealed off close to the bulb on the 4-mm base of the capillary. A fairly small soft flame was used to prevent the vacuum from sucking a hole in the seal. The sample was again shaken to the very tip of its capillary, which was sealed off at the desired length by the use of a micro flame.

Successive samples were prepared by shaking the hydride back from the other capillaries into the main bulb, reconnecting the bulb to the vacuum system, heating the furnace to the proper temperature, and removing the desired amount of hydrogen. The hydrogen removed was measured by water displacement from a Mariotte bottle as previously described.

Decomposition of ThH_2 requires a high vacuum at the highest temperature pyrex will stand (about 575°C), and the hydrogen removal in this region must be done with a great deal of care to avoid collapsing the sample bulb and attached capillaries.

3.2 X-ray Studies of the Thorium-Hydrogen System. Samples prepared as described above were examined by x-ray diffraction. The phases found at various hydrogen compositions are recorded in Table 2, along with the relative intensity of the maxima of the phases. The latter are roughly a measure of the relative proportions of the observed phases.

The x-ray evidence indicates that the composition of phase A lies between $\text{ThH}_{1.78}$ and $\text{ThH}_{2.11}$, whereas the composition of phase B must be greater than ThH_3 . Phase A, the lower hydride, is isomorphous with ThC_2 (see below), and hence there is good reason to believe that the composition is ThH_2 on x-ray grounds alone. The chemical work presented above also supports this composition, so that there is little doubt that the ideal composition of the lower hydride is ThH_2 .

Phase B is identical with Zachariasen's hydride. Neither x-ray data nor chemical data, however, give an unequivocal answer to the question of the composition of the higher hydride, though it is greater than ThH_3 , as previously reported,⁵ and may be either $\text{ThH}_{3.75}$ or ThH_4 . This question is discussed in more detail below. It is concluded that the composition $\text{ThH}_{3.75}$ is possibly the more likely.

X-ray diagrams of both lower and higher hydrides are too diffuse for precision determinations of the lattice constants, so x-ray data on the solid solubility of the hydrides with each other or with thorium are meager. Variability of the spacing of the higher hydride is great enough to suggest solid solubility or solubility of hydrogen in the higher hydride, but poor correlation of the hydride spacing with hydrogen composition may mean that impurities in the metal and hydride are responsible for the variability of the hydride spacing (Table 3).

3.3 The Structure of ThH_2 . Reflections at low scattering angles of ThH_2 may be indexed on the basis of a body-centered tetragonal unit (Table 4), $a = 4.09 \pm 0.03$ Å, $C = 5.02 \pm 0.03$ Å, $Z = 2$, $\rho = 8.36$. Maxima at higher angles cannot be measured with accuracy, but the measurements are sufficiently accurate to indicate that the above unit is a pseudo unit.

The pseudo unit and structure of ThH_2 are quite like the ThC_2 unit and structure reported in the literature.⁸ Recently this laboratory reinvestigated the structure of ThC_2 , and it appears that the reported structure of ThC_2 is a pseudo structure. It is believed that ThH_2 and ThC_2 are isomorphous, and, since better x-ray data can be obtained from ThC_2 , the structure will be reported when the investigation of ThC_2 is complete.

For the present it appears that the pseudo structure reported above is a very close approximation. (It may be that ThC_2 and ThH_2 are orthorhombic with $a \approx b$.) The pseudo structure is represented in Fig.

7. There are 14 thorium neighbors about each thorium atom, 8 at 3.83 Å, 2 at 4.09 Å, 4 at 5.02 Å. (The packing would be cubic closest-packed if $a = c$.)

The hydrogen positions are a matter of speculation as far as the x-ray data are concerned. The ThC_2 structure has, however, been interpreted in terms of C_2 radicals arranged normal to the c axis of the unit, as shown in Fig. 7. This accounts in a satisfactory way for the fact that the c axis is approximately equal to the cubic edge of thorium metal, whereas the other two dimensions have been expanded. A similar structure may be presumed for the hydride. In terms of a face-centered unit the metal has $a = b = c = 5.07$ Å, whereas the hydride has $a = b = 5.78$ Å, $c = 5.02$ Å.

Zirconium hydride (ZrH_2) and ZrC_2 are reported to have structures isomorphous with that of ThC_2 .⁹

Ignoring Lorentz polarization, adsorption, and other factors which change continuously and fairly slowly with angle, the intensity of the maxima from ThH_2 should be proportional to the multiplicity factor. In Table 4, multiplicity factors are given for the observed maxima assuming a tetragonal unit. In general, the observed intensities of neighboring maxima are proportional to the multiplicity factor, but there are some exceptions. This is not surprising since the given structure is a pseudo structure.

Some reflections beyond those listed in Table 4 have been measured. The measurements at higher angles are not reliable and are not listed. The pseudo unit becomes increasingly unsatisfactory in accounting for both the number and positions of maxima observed at greater angles.

X-ray spacings for ThH_2 are so unreliable that nothing certain can be said about the solubility of thorium or higher hydride in ThH_2 on the basis of x-ray data alone. Vapor-pressure data on this point are discussed in Sec. 4.

3.4 The Higher Thorium Hydride. Zachariasen has presented a detailed account of the x-ray data and the structure of the higher hydride. In brief his results are as shown in Table 4.

The hydride is body-centered cubic, $a_0 = 9.09 \pm 0.02$ Å. There are 16 Th atoms per unit, so that $\rho = 8.25$, assuming 3 hydrogen atoms per thorium atom. The thorium positions are

$$(0\ 0\ 0) \frac{(1\ 1\ 1)}{2\ 2\ 2} + (x\ x\ x), (x + \frac{1}{4}, x + \frac{1}{4}, x + \frac{1}{4}), \\ (x + \frac{3}{4}, \frac{1}{4} - x, \frac{3}{4} - x), (x + \frac{1}{2}, \frac{1}{2} - x, \bar{x})$$

with $x = 0.215 \pm 0.010$.

In Table 2 evidence is presented that the composition of the higher hydride is greater than ThH_3 . In Sec. 2 chemical evidence indicates that the hydrogen-thorium ratio is greater than 3.5. Since the ideal composition is complicated by the impurity of the thorium metal, particularly with respect to oxide, it is difficult to determine the ideal composition chemically. It is interesting in this regard to examine the x-ray evidence.

The positions which Zachariasen has found for the Th atoms are 16 equivalent positions limited to the space group $T^6d-143d$. The positions available to hydrogen therefore almost certainly conform to this space group. By suitable choice of combinations of the 12-, 16-, 24-, and 48-fold positions of T^6d , hydrogen sites can be chosen for 48, 52, 56, 60, 64 and higher numbers of hydrogen atoms. These correspond to ThH_3 , $\text{ThH}_{3.25}$, $\text{Th}_{3.5}$, $\text{Th}_{3.75}$, and ThH_4 . Ratios between these values cannot correspond to the ideal composition of the hydride. Since compositions well over $\text{ThH}_{3.5}$ have been achieved, it appears that the ideal composition is either $\text{ThH}_{3.75}$ or ThH_4 , requiring sites for 60 or 64 hydrogen atoms. These cannot be distinguished on the basis of x-ray data, but if the maximum observed composition is lower than the theoretical composition because of impurities in the metal, the ideal composition $\text{ThH}_{3.75}$ (60 H atoms per unit) seems the more likely. The highest composition of thorium hydride thus far prepared is $\text{ThH}_{3.62}$. The largest impurity in the thorium used is oxide, estimated to be 2 per cent or so. All impurities are certainly too small to be responsible for cutting the H-Th ratio from 4 to 3.62, though they are of a magnitude to cut the ratio from 3.75 to 3.62.

It has previously been reported that the higher hydride has a variable x-ray spacing.¹⁰ Recently an examination of the spacing as a function of hydrogen content was made, and a summary is presented in Table 3. It is unfortunate that the x-ray maxima are too diffuse to permit a more exact determination of the lattice constant. However, no direct relation between composition and lattice constant can be established, and it seems likely that the impurities in the metal and hydride are responsible for the variations observed. It is possible that oxygen (or oxide) influences the spacing, since some correlation has been noted between the oxygen content of the thorium and the spacing of the hydride prepared from it.

4. DISCUSSION

4.1 The Nature of ThH_2 . The structure of ThH_2 has been shown to be very similar to, if not isomorphous with, the structure of ThC_2 and ZrC_2 . The latter compounds are generally classed as interstitial

compounds or interstitial solid solutions. They are derived from a cubic closest-packed metal structure by introducing C_2 radicals into the octahedral interstices. In the ThC_2 structure the C_2 radicals are all parallel to a single cubic face, and alternate C_2 radicals are at right angles to each other and at 45-deg angles with two of the cube axes (Fig. 7). This increases these two axes, so that the resultant structure is tetrahedral.

At the composition ThC_2 all the octahedral interstices are occupied by C_2 groups. Similarly at ThH_2 all the octahedral interstices should be filled with H_2 groups, but the lower hydride phase should be stable over a considerable composition range of lower hydrogen content if ThH_2 is to be regarded as an interstitial solid solution. Actually the composition range of the lower hydride phase seems rather narrow, from both x-ray and vapor-pressure studies (Table 2 and Figs. 2 and 3).

What variation there is in the composition of the lower hydride phase seems to increase with temperature. Thus from Fig. 4 it appears that, as the temperature is increased, the lower hydride phase becomes stable at lower hydrogen contents. Because of this there is a greater ratio of pressures at two different temperatures at the higher hydrogen compositions, and consequently ΔH (formation) of ThH_2 appears to decrease (becomes more negative) with composition, as noted in Sec. 2.2.

It has been assumed, because of the similarity of ThC_2 and ThH_2 , that H_2 groups are involved in the lower hydride structure. Actually the evidence for H_2 groups is slight, since even for the carbides having a ThC_2 structure the positions of the carbon atoms are mostly a matter of conjecture. Indeed, it is difficult to understand the nature of the H_2 groups, if they exist. The lower hydride does not appear to be a solution of hydrogen molecules in thorium metal. If the H_2 group is an ion, it should presumably possess a negative charge, yet H_2^{--} is impossible, and H_2^- would require a rather unstable and rare three-electron bond.

4.2 The Higher Thorium Hydride. The higher thorium hydride has a structure unrelated to that of the metal. In this case there is no doubt that the hydride is a true compound. Nevertheless, it appears that the higher hydride may be stable over a moderate composition range.

X-ray diagrams of hydrides of over-all composition above $ThH_{3.2}$ appear to be one phase (Table 2). Decomposition and formation pressures of the higher hydride diverge quite widely, and both decomposition and formation pressures at a given temperature increase with hydrogen content of the higher hydride. As in the case of the lower

hydride, the composition range of stability of the higher hydride seems to increase with temperature, leading to an apparent increase of ΔH (formation) with composition (Table 1).

Table 1—Heat of Formation of Thorium Hydride

Reaction	Composition (H/Th)	ΔH , cal/mole	
		At composition stated	Average
$\text{Th} + \text{H}_2 = \text{ThH}_2$	0.5	- 34,720	- 35,200
	1.5	- 35,670	
$\text{ThH}_2 + \left(\frac{x}{2} - 1\right) \text{H}_2 = \text{ThH}_x$	2.4	- 19,120	- 19,300
($x = 3.75$ or 4)	3.2	- 19,490	

Table 2

Composition	Phases and intensity
$\text{ThH}_{0.82}$	Th (medium) + A (medium)
$\text{ThH}_{1.24}$	Th (weak) + A (medium)
$\text{ThH}_{1.50}$	Th (weak) + A (strong)
$\text{ThH}_{1.78}$	A
$\text{ThH}_{1.98}$	A
$\text{ThH}_{2.11}$	A (strong) + B (very weak)
$\text{ThH}_{2.49}$	A (medium) + B (medium)
$\text{ThH}_{2.56}$	A (medium) + B (medium)
$\text{ThH}_{2.98}$	A (weak) + B (strong)
$\text{ThH}_{3.12}$	A (weak) + B (strong)
$\text{ThH}_{3.53}$	B
$\text{ThH}_{3.62}$	B

Table 3—Higher Hydride Lattice Constant vs. Composition

Composition	Lattice constant, A
ThH _{2.49}	9.10 ± 0.02
ThH _{2.558}	9.12 ± 0.02
ThH _{2.66}	9.110 ± 0.02
(ThH ₃)	9.09 ± 0.02
	(reference 5)
ThH _{3.115}	9.10 ± 0.02
ThH _{3.25}	9.12 ± 0.02
ThH _{3.40}	9.13 ± 0.02
ThH _{3.50}	9.17 ± 0.02
ThH _{3.53}	9.10 ± 0.02
ThH _{3.62}	9.10 ± 0.02
ThH _x *	9.14 ± 0.02
ThH _x †	9.15 ± 0.02

*Prepared at 1800 psi H₂.

†From Hg amalgam.

Table 4—Observed X-ray Maxima for ThH₂. Sin² θ Values for CuK Alpha Radiation

Indices*	Sin ² θ		Intensity†	Multiplicity factor
	Observed	Calculated		
(101)	0.0602	0.0596	VS	8
(110)	0.0727	0.0722	M	4
(002)	0.0940	0.0938	W	2
(200)	0.1449	0.1444	M~	4
(112)	0.1660	0.1660	M	8
(211)	0.2055	0.2040	MS	16
(202)	0.2379	0.2382	M	8
(103)	0.2469	0.2462	W	8
	0.3138			
(301)	0.3480	0.3483	W	8
	0.3570			
(004)	(0.3778)?	0.3752	(VWV)?	2
(222)	0.3808	0.3826	VW	8
(213)	0.3916	0.3916	M	16
	0.4259			
(312)	0.4540	0.4548	M	16
(321)	0.4934	0.4928	M	16

*For body-centered, tetragonal unit.

†W, weak; VW, very weak; VWV, very very weak; M, medium; MS, medium strong; VS, very strong.

Fig. 1 — Apparatus for measuring the dissociation pressures in the thorium-hydrogen system.

Fig. 2 — Pressure isotherms for the thorium-hydrogen system.

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Fig. 3—Isotherms for the hydrogen-thorium system.

Fig. 4—Dissociation pressures of the Th-ThH₂ system at various temperatures.

Fig. 5—Dissociation pressures of the ThH_2 - ThH_x system ($x = 3.75$ or 4) at various temperatures.

Fig. 6 — Apparatus for the preparation of thorium hydride samples for x-ray studies.

Fig. 7 — Approximate structure of thorium hydride (ThH_2). The positions of the H_2 radicals are doubtful, but they are chosen to correspond to the proposed carbon positions in the isomorphous ThC_2 structure.

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Paper 7.7

COMPLEX IONS FORMED BY THORIUM AND IRON WITH
FLUORIDE IN ACID SOLUTION

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1. INTRODUCTION

Fluoride ion has long been known to form complex ions with many cations, e.g., Al^{+3} , Fe^{+3} , and ZrO^{++} . This can be demonstrated qualitatively by dissolving a precipitate of lanthanum fluoride in a solution containing one of the above cations.

Since the purpose of this paper is to present results on the complexing of ferric ions and thorium ions by fluoride in acid solution, it is of interest to examine the evidence for complexing of ferric iron by fluoride.

Peters¹ measured the freezing point and electrical conductivity of ferric fluoride solutions and concluded that FeF_3 was almost undissociated. The observed molecular weights of FeF_3 from the freezing points of solutions containing 1.921 and 0.954 g of FeF_3 per 100 g of H_2O were 118.2 and 112.7, respectively; the theoretical molecular weight of FeF_3 is 113. The molar conductivities at dilutions of 6 and 96 liters/mole were 10.0 and 24.2 reciprocal ohms per centimeter, respectively.

Other evidences for almost no dissociation of FeF_3 are the absence of, or the very great inhibition of, the reaction of ferric ion with $\text{Fe}(\text{CN})_6^{-3}$ and CNS^- ; the hydrolysis of ferric ion; and the precipitation of calcium fluoride.²

Petersen³ observed a heat effect of 0.58 Kcal/mole of FeF_3 when HF was added to neutral ferric fluoride solution. He attributed this to the formation of a ferric fluoride anion or a weak acid of such an ion. Peters¹ found that the electrical conductivity of a solution containing

NaF and FeF_3 was less than that of the separate solutions and that in a solution of Na_3FeF_6 the iron moved with the fluoride toward the anode. The observation² that some of the chemical reactions of ferric ion are even more suppressed in an NaF- FeF_3 solution than in pure FeF_3 solutions could be explained by the shifting of an equilibrium, but the experiments cited above do seem to indicate the existence of a ferric fluoride anion. The existence of solid salts of the type $\text{Me}^{\text{I}}(\text{FeF}_4)$, $\text{Me}_2^{\text{I}}(\text{FeF}_5)$, and $\text{Me}_3^{\text{I}}(\text{FeF}_6)$ is an indication, but not a proof, that ferric fluoride anions exist in aqueous solution.

Low and Pryde⁴ developed a microanalytical procedure for fluoride based on the change of potential of an Fe^{+3} - Fe^{++} half cell when fluoride was added. They found that the cells behaved very well and that the potential change for a given amount of fluoride added was very reproducible. They noticed that their data could not be accounted for by the formation of FeF_6^{-3} and failed to notice that it could be accounted for quantitatively by the assumption of the equilibrium

The value of K_1 calculated from their data is 162. This may be compared with the value 189 which was determined in the research reported here. Both constants are for an ionic strength of 0.5; however, Low and Pryde's experiments were done in 0.5M KCl plus 0.01M HCl, and thus the analysis of the data involved large corrections for hydrolysis and chloride complexing of the ferric ions, which introduces an uncertainty of about 25 per cent in the K_1 . The experiments in this work were carried out in NaClO_4 - HClO_4 solutions.

In this paper the potential of the Fe^{+3} - Fe^{++} electrode is studied as a function of the HF and H^+ concentration, and it is shown that the data can be interpreted quantitatively by assuming the existence of the complexes FeF^{++} , FeF_2^+ , and FeF_3 .

While developing a method of analysis for thorium based on the precipitation of thorium fluoride, it was noticed that thorium apparently formed complex ions with fluoride. The procedure being used was the titration with NaF of a solution containing Th^{+4} , Fe^{+3} , and Fe^{++} and the measurement of the potential of a gold electrode inserted in the solution. When the precipitation of $\text{ThF}_4 \cdot 4\text{H}_2\text{O}$ was complete, the potential would change suddenly by a large amount owing to the complexing of Fe^{+3} by the excess fluoride. During the titration there was no precipitate formed, and there was only a very small change in potential up to the point where about 2 moles of NaF per mole of Th^{+4} had been added. At this point a precipitate started forming, and there was a discontinuity in the potential; the potential then changed continuously until the big change at the end point. When the titration was

finished, thorium nitrate was added to the solution until there was slightly less than 2 moles of fluoride per mole of thorium; the precipitated thorium fluoride dissolved after stirring and heating, and a light beam passed through the solution showed no Tyndall effect. This seemed to be very good evidence for the existence of a thorium fluoride complex.

After the Fe^{+3} - Fe^{++} electrode had been studied, it was possible to interpret the data for cells containing thorium by assuming the existence of the complex ions ThF^{+3} , ThF_2^{++} , and ThF_3^+ . The solubility product of $\text{ThF}_4 \cdot 4\text{H}_2\text{O}$ was also determined.

2. EXPERIMENTAL PROCEDURE

The type of cell used for the electrometric titrations is shown in Fig. 1. The containers R and F and the caps with entrances for the stirrers, etc., were made from large ground-glass joints of about 5 cm diameter. The containers held about 100 cc of solution when filled to the level shown in the diagram.

The gold electrodes were made of gold sheet and gold wire; they had a surface area of about 8 cm^2 . After they had been made, they were cleaned with warm aqua regia, and it was found that it was not necessary to clean them again. When not in use, they were stored in distilled water.

The two halves of the cell were connected by means of an agar-agar- NaClO_4 salt bridge. The NaClO_4 solution used in making the salt bridges was 1.6M. The high salt concentration in the salt bridge was used in an effort to minimize junction potentials. In order to eliminate effects due to junction potentials, the two halves of the cell were always identical in composition initially. In order to minimize the change in composition of the side which was being titrated, the total volume of solution added was only 5 cc as compared to 100 cc for the initial volume. In a typical experiment (data in Table 5) the initial composition was 0.398M NaClO_4 , 0.111M HClO_4 ; and the final composition was 0.395M NaClO_4 , 0.090M HClO_4 , 0.016M HF. A net junction potential of 0.7 mv was calculated from the Henderson equation⁵ for the two junctions:

$$\begin{array}{l} \text{NaClO}_4 = 0.398\text{M} \\ \text{HClO}_4 = 0.111\text{M} \end{array} \left| \text{NaClO}_4 = 1.61\text{M} \right| \begin{array}{l} \text{NaClO}_4 = 0.395\text{M} \\ \text{HClO}_4 = 0.090\text{M} \end{array}$$

This result indicates that the junction potentials were probably negligible.

The buret used for adding the NaF solution had a capacity of 5 cc with 0.02-cc divisions. As a result of the comparison of two succes-

sive calibrations it is believed that the volumes added were accurate to ± 0.002 cc for volumes up to 1.5 cc and ± 0.005 cc for volumes from 1.5 to 5 cc. The tip of the buret was made from capillary tubing. In actual operation the meniscus was set on one of the lines, and the tip of the buret was dipped in the solution after each addition.

Since ferrous iron is slowly oxidized by oxygen of the air, an inert atmosphere of CO_2 was kept over the solutions in the cells. A CO_2 generator was made by placing solid CO_2 in a Dewar flask. The CO_2 from the generator was bubbled through a solution of the same composition and at the same temperature as the solution in the cells. The degree of oxidation over a period of several hours was checked by titration with Ce^{+4} and was found to be less than 1 per cent.

The stock sodium perchlorate solution was prepared by weighing, dissolving in distilled water, and diluting to a known volume in a volumetric flask G. Frederick Smith Chemical Company's anhydrous NaClO_4 . For keeping the ionic strength constant, NaClO_4 was used, instead of LiClO_4 or KClO_4 , because LiF is only sparingly soluble and KF forms double salts with thorium fluoride.⁶ Also NaF apparently does not form double salts with thorium fluoride.⁶

The HClO_4 stock solution was prepared by diluting G. Frederick Smith Chemical Company's 70 per cent HClO_4 . The stock solution was standardized by titration against Na_2CO_3 , HgO with KI , and NaOH which had been standardized against potassium acid phthalate. The three methods agreed within 1 per cent; the HgO value was taken as the most reliable, and it is believed it was valid to ± 0.1 per cent.

The ferrous-ferric perchlorate solutions were prepared from G. Frederick Smith Chemical Company's ferrous perchlorate. A solution containing 0.1M HClO_4 and 0.1M $\text{Fe}(\text{ClO}_4)_2$ was prepared, and then the ferrous iron was partially oxidized to ferric iron with H_2O_2 . The ferrous iron concentration was determined by titration with KMnO_4 which had been standardized against $\text{Na}_2\text{C}_2\text{O}_4$. The total iron concentration was determined by the Zimmermann-Reinhardt method; the difference between the total iron and the ferrous iron concentrations was taken as the ferric iron concentration. The acid concentration in the ferrous-ferric perchlorate solution was determined by the procedure developed by Schumb, Sherrill, and Sweetser.⁷ The ferrous-ferric solution was always opened in a CO_2 atmosphere in order to prevent oxidation by atmospheric oxygen. A solution which had been opened many times over a period of two months was reanalyzed for ferrous iron and found to agree within 0.1 per cent with the original analysis. It is believed that the Fe^{++} and Fe^{+3} concentrations were good to 0.1 per cent and the HClO_4 concentration was good to 0.3 per cent.

The sodium fluoride used was prepared by distilling concentrated HF from a platinum still onto C.P. NaHCO_3 in a platinum crucible. The material in the crucible was evaporated to dryness on a steam bath, ground in a mortar, heated to 300°C for 2 hr, and then stored in a desiccator. The standard solutions were prepared by weighing the anhydrous NaF, dissolving the NaF in distilled water, diluting to a known volume, and then storing in a wax-lined bottle.

After several attempts to prepare thorium perchlorate failed, it was decided to use thorium nitrate. A good-quality thorium nitrate was ground to a powder in a mortar and then weighed, dissolved in distilled water, and diluted to a known volume. At the same time aliquots of the solid were weighed into crucibles and ignited to ThO_2 in order to determine accurately the percentage of thorium in the solid.

The procedure for carrying out a titration was as follows: The containers R and F were filled by transferring the desired volumes of the stock solutions with calibrated pipets. The HClO_4 concentration varied from about 0.03M to about 0.3M; enough sodium perchlorate solution was always added to make the ionic strength approximately 0.5. Enough distilled water was added each time to make the initial volume about 100 cc. After the NaClO_4 , HClO_4 , and H_2O had been added, the caps with the stirrers and electrodes in position were placed on the containers; the two halves of the cells were connected with the agar-agar salt bridge; and the whole cell was placed in a thermostat regulated at $25.00 \pm 0.01^\circ\text{C}$. After the air had been swept out of the upper part of the cells by CO_2 , the ferrous-ferric perchlorate was pipetted into each half of the cell. The stirrers were started, and the potential of the cell was followed for $\frac{1}{2}$ to 2 hr. In principle the initial potential of the cell should have been zero, but in almost every case a potential of from 0.1 to 0.5 mv was observed. The titration was not started until this small potential had remained constant for 20 to 30 min. After the initial potential had become constant, the buret was placed in position, the stirrer was started, and an aliquot of NaF solution was added. The stirrer was shut off after it had been running 5 to 7 min, and the potential of the cell was measured with a Leeds & Northrup type K potentiometer. The readings were very steady and showed no signs of drifting. The average time between additions of an aliquot was 8 to 10 min.

The experimental results on cells which contained no thorium are given in columns 1 and 2, Tables 2 to 7. The curves in Fig. 2 are graphs of the data in Tables 2, 3, 6, and 7. They demonstrate the effect of acid concentration on the variation of ΔE with HF concentration.

The procedure for carrying out a titration for a cell with thorium present was identical with the procedure when no thorium was present. The experimental results for cells with varying concentration of thorium nitrate are given in columns 1 and 2, Tables 8 to 11. All the experiments with thorium in the cells were carried out with an acid concentration of approximately 0.05. In Fig. 3 graphs of the data for cells with various thorium concentrations are given. The upper curve is a graph of the data in Table 4, a titration with $[H^+]_0 \approx 0.05$ and with no thorium present.

In order to make sure that CO_2 had no effect on the $Fe^{+3}-Fe^{++}$ potential, a cell was prepared in which one side was swept out with nitrogen and CO_2 was bubbled in the other side. The CO_2 had no effect on the potential.

3. ANALYSIS OF THE DATA FOR IRON

In analyzing the data it is necessary to consider the following equilibria:

In the above equilibrium constants, brackets are used to designate concentrations in moles per liter. Activity coefficients are included in the K ; e.g., $K_1 = K_1^0 \frac{\gamma(HF) \gamma[Fe(ClO_4)_3]}{\gamma[(FeF)(ClO_4)_2] \gamma(HClO_4)}$ where K_1^0 is the equilibrium constant at zero ionic strength. All the experiments were performed at an ionic strength of 0.5, this value being chosen because most electrolytes have a small rate of change of activity coefficient with ionic strength at this ionic strength⁸ and because Bray and Hershey⁹ have shown that equilibria of the type in Eq. 3 show almost no rate of change with ionic strength at $\mu = 0.5$.

At the acid concentrations used in the experiments, equilibria 3, 4, and 5 are shifted predominantly to the left and hence enter into the analysis of the data more or less as "corrections"; because of this fact it is not necessary to know the values of these constants with high accuracy. Two values of K_H^0 are given in the literature; $K_H^0 = 0.0060$ was reported by Bray and Hershey,⁹ and $K_H^0 = 0.0035$ was reported by Lamb and Jacques.¹⁰ Bray and Hershey's value was chosen arbitrarily. When it is corrected to $\mu = 0.5$ by means of the activity coefficient function also given by Bray and Hershey, $K_H = 0.00185$. Roth¹¹ reviewed the literature, studied equilibria 4 and 5, and gave $K_4^0 = 0.00024$ and $K_5^0 = 33$ as the best values for these constants. By assuming that $\gamma(\text{HF}) = 1$ and $\gamma \pm (\text{HF}) = \gamma \pm (\text{HCl})$, $K_4 = 0.00042$ at $\mu = 0.5$ was estimated. Since ΔZ^2 for equilibrium 5 is zero, $K_5 = 33$ was used at $\mu = 0.5$.

Equilibria 1 and 2 are assumed to exist, and it will be shown that the data can be interpreted quantitatively on the basis of these equilibria. It is also assumed that Fe^{++} is not complexed by fluoride ion. This assumption and the possibility of interpreting the data by assuming equilibria other than 1 and 2 will be discussed at the end of this section.

It will be noted that equilibria 1 and 2 are not volume dependent, whereas equilibria 3, 4, and 5 are volume dependent. During the titration the volume increased by 5 per cent. This change is within the accuracy of K_H , K_4 , and K_5 , and it is therefore neglected. All concentrations were calculated with respect to the initial volume.

The quantities observed in a titration are $[\text{F}^-]_T$, the total concentration of fluoride in the solution, and $\Delta E = E - E_0$, where E_0 is the potential of the half cell when no fluoride is present and E is the potential when the total concentration of fluoride is $[\text{F}^-]_T$. The initial hydrogen ion concentration $[\text{H}^+]_0$ and the total ferric iron concentration $[\text{Fe}^{+3}]_T$ are also known. The concentration of ferric ions $[\text{Fe}^{+3}]$ may be calculated as follows:¹²

$$E = E^0 - \frac{RT}{nF} \ln \frac{[\text{Fe}^{+3}] \gamma [\text{Fe}(\text{ClO}_4)_3]}{[\text{Fe}^{++}] \gamma [\text{Fe}(\text{ClO}_4)_2]} \quad (6)$$

$$E_0 = E^0 - \frac{RT}{nF} \ln \frac{[\text{Fe}^{+3}]_0 \gamma [\text{Fe}(\text{ClO}_4)_3]}{[\text{Fe}^{++}] \gamma [\text{Fe}(\text{ClO}_4)_2]} \quad (7)$$

Since the ionic strength is the same and the composition of the solution has changed only slightly, the activity coefficients will be essentially equal in Eqs. 6 and 7. Since it has been assumed that ferrous ion is not complexed by fluoride, the Fe^{++} concentration will be the same in Eqs. 6 and 7. Subtracting Eq. 7 from Eq. 6

$$\Delta E = E - E_0 = \frac{-RT}{nF} \ln \frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+3}]_0} \quad (8)$$

Changing to base 10 logarithms and taking $\frac{RT}{nF} \ln 10 = 59.14$ mv at 25°C

$$\log \frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+3}]_0} = \frac{-\Delta E}{59.14} \quad (9)$$

where ΔE is in millivolts.

The concentration of ferric ions when no fluoride is present, $[\text{Fe}^{+3}]_0$, is not equal to $[\text{Fe}^{+3}]_T$ because the solutions contain FeOH^{++} . By considering equilibrium 3 it is found that

$$\frac{[\text{Fe}^{+3}]_T}{[\text{Fe}^{+3}]_0} = 1 + \frac{K_H}{[\text{H}^+]_0} \quad (10)$$

From Eqs. 9 and 10, $[\text{Fe}^{+3}]/[\text{Fe}^{+3}]_T$, the fraction of the total ferric iron present as ferric ions, can be calculated as a function of $[\text{F}^-]_T$. The ratios $[\text{Fe}^{+3}]/[\text{Fe}^{+3}]_T$ and $[\text{F}^-]_T/[\text{Fe}^{+3}]_T$ are given for the various experiments in columns 3 and 5, respectively, of Tables 2 to 7.

In order to obtain the concentration of ferric iron present as fluoride complexes, $[\text{Fe}^{+3}]_C$,

$$\frac{[\text{Fe}^{+3}]_C}{[\text{Fe}^{+3}]_T} = 1 - \left\{ \frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+3}]_T} + \frac{[\text{FeOH}^{++}]}{[\text{Fe}^{+3}]_T} \right\} \quad (11)$$

is derived from the stoichiometric relation for iron, and by considering equilibrium 3

$$\frac{[\text{Fe}^{+3}]_C}{[\text{Fe}^{+3}]_T} = 1 - \left\{ 1 + \frac{K_H}{[\text{H}^+]} \right\} \frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+3}]_T} \quad (12)$$

Since $K_H/[\text{H}^+]$ had a maximum value of 0.057 and $[\text{H}^+]$ changed by only 4 per cent for the experiment at the lowest hydrogen ion concentration (see Table 2), the quantity $\left\{ 1 + \frac{K_H}{[\text{H}^+]} \right\}$ was constant to within 0.3 per cent. For the experiments at higher acid concentration the change in this quantity was of a similar order of magnitude or smaller; hence

$$1 + \frac{K_H}{[\text{H}^+]} \approx 1 + \frac{K_H}{[\text{H}^+]_0} \quad (13)$$

Combining Eqs. 13 and 10 and inserting the result in Eq. 12

$$\frac{[\text{Fe}^{+3}]_C}{[\text{Fe}^{+3}]_T} = 1 - \frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+3}]_0} \quad (14)$$

This quantity is given in column 4, Tables 2 to 7.

In order to calculate K_1 and K_2 , $[\text{HF}]$, as well as the distribution of $[\text{Fe}^{+3}]_C$ between $[\text{FeF}^{++}]$ and $[\text{FeF}_2^+]$, must be known; since these quantities depend upon the values of K_1 and K_2 , it is necessary to use a method of successive approximations. In principle a graph could be made of $[\text{Fe}^{+3}]_C$ against $[\text{F}^-]_T$, and K_1 and K_2 could then be determined by fitting a curve to the points, but it is easier to use a method of successive approximations in this case.

From stoichiometric considerations

$$[\text{F}^-]_T = [\text{HF}] + [\text{F}^-] + 2[\text{HF}_2^-] + [\text{FeF}^{++}] + 2[\text{FeF}_2^+] \quad (15)$$

and when equilibria 4 and 5 are applied

$$[\text{HF}] \left\{ 1 + \frac{K_4}{[\text{H}^+]} + 2K_4K_5 \frac{[\text{HF}]}{[\text{H}^+]} \right\} = [\text{F}^-]_T - \left\{ [\text{FeF}^{++}] + 2[\text{FeF}_2^+] \right\} \quad (16)$$

From equilibrium 2 the relation

$$[\text{FeF}^{++}] + 2[\text{FeF}_2^+] = [\text{Fe}^{+3}]_C \frac{\left\{ 1 + 2K_2 \frac{[\text{HF}]}{[\text{H}^+]} \right\}}{\left\{ 1 + K_2 \frac{[\text{HF}]}{[\text{H}^+]} \right\}} \quad (17)$$

may be derived. When Eq. 17 is inserted into Eq. 16

$$[\text{HF}] \left\{ 1 + \frac{K_4}{[\text{H}^+]} + 2K_4K_5 \frac{[\text{HF}]}{[\text{H}^+]} \right\} = [\text{F}^-]_T - [\text{Fe}^{+3}]_C \frac{\left\{ 1 + 2K_2 \frac{[\text{HF}]}{[\text{H}^+]} \right\}}{\left\{ 1 + K_2 \frac{[\text{HF}]}{[\text{H}^+]} \right\}} \quad (18)$$

The quantity $\left\{ 1 + \frac{K_4}{[\text{H}^+]} + 2K_4K_5 \frac{[\text{HF}]}{[\text{H}^+]} \right\}$ shall be designated by α . Under the experimental conditions used, this quantity ranged from 1.002 to 1.024, and for any given experiment it was very nearly a constant, as may be seen by inspection of column 9, Tables 2 to 7. For this reason Eq. 18 may be written in the simplified form

$$[\text{HF}]\alpha = [\text{F}^-]_{\text{T}} - [\text{Fe}^{+3}]_{\text{C}} \frac{\left\{ 1 + \frac{2K_2}{\alpha} \frac{[\text{HF}]\alpha}{[\text{H}^+]} \right\}}{\left\{ 1 + \frac{K_2}{\alpha} \frac{[\text{HF}]\alpha}{[\text{H}^+]} \right\}} \quad (19)$$

where α is very nearly unity and a constant for any given experiment.

From equilibria 1 and 2

$$K_2 = \frac{1}{K_1} \frac{[\text{Fe}^{+3}]_{\text{C}}}{[\text{Fe}^{+3}]} \frac{[\text{H}^+]^2}{[\text{HF}]^2} - \frac{[\text{H}^+]}{[\text{HF}]} \quad (20)$$

may readily be obtained; by dividing through by α

$$\frac{K_2}{\alpha} = \left(\frac{\alpha}{K_1} \right) \frac{[\text{Fe}^{+3}]_{\text{C}}}{[\text{Fe}^{+3}]} \frac{[\text{H}^+]^2}{[\text{HF}]^2\alpha} - \frac{[\text{H}^+]}{[\text{HF}]\alpha} \quad (21)$$

From the stoichiometric relation for hydrogen ion

$$[\text{H}^+] = [\text{H}^+]_0 - [\text{HF}] \quad (22)$$

A first approximation to $[\text{HF}]\alpha$ was obtained from the equation

$$[\text{HF}]\alpha \approx [\text{F}^-]_{\text{T}} - [\text{Fe}^{+3}]_{\text{C}} \quad (23)$$

This gives $[\text{HF}]\alpha$ to within 10 per cent as may be seen by comparing columns 4, 5, and 6, Tables 2 to 7. The first approximation to K_1/α was obtained from a graph of $2[\text{Fe}^{+3}]_{\text{C}} - [\text{F}^-]_{\text{T}}$ against ΔE . The equation

$$2[\text{Fe}^{+3}]_{\text{C}} - [\text{F}^-]_{\text{T}} = [\text{HF}]\alpha \left\{ \frac{K_1[\text{Fe}^{+3}]}{\alpha[\text{H}^+]} - 1 \right\} \quad (24)$$

may be derived from equilibrium 1 and the stoichiometric relation

for fluoride. From this equation it is apparent that $\frac{K_1}{\alpha} = \frac{[\text{H}^+]}{[\text{Fe}^{+3}]}$ when

$2[\text{Fe}^{+3}]_{\text{C}} - [\text{F}^-]_{\text{T}}$ is zero. This procedure gives a value of K_1/α within 2 per cent of the final adjusted value. Having a good value of K_1/α and approximate values of $[\text{HF}]\alpha$, Eqs. 21 and 22 were used to obtain an approximate value of K_2/α . Next, Eq. 19 was applied to obtain better values of $[\text{HF}]\alpha$, and then the procedure for obtaining K_2/α was repeated. Finally K_1/α was adjusted slightly to make K_2/α as constant as possible. In practice it was found that the third approximation to $[\text{HF}]\alpha$ was practically identical with the second approximation to $[\text{HF}]\alpha$; this rapid convergence is due to the fact that $[\text{HF}]\alpha$ is comparatively

insensitive to a change in K_2/α . The physical reason for this rapid convergence is the fact that most of the fluoride added to the solution simply reacts with hydrogen ion to form HF; a small percentage reacts with ferric ions to form complexes, and a very small percentage is present as F^- ions and HF_2^- ions.

The values of $\frac{[HF]\alpha}{[Fe^{+3}]_T}$, $\frac{[H^+]}{[Fe^{+3}]_T}$, and $\frac{K_2}{\alpha}$ calculated by successive approximations are given in columns 6, 7, and 8, respectively, of Tables 2 to 7. The corresponding adjusted value of K_1/α is given at the top of the table. It will be noted that the first three or four values of K_2/α are not very accurate. The physical reason for this is that most of the ferric iron in this region is present as FeF^{++} , the relative amount of FeF_2^+ being very small. Mathematically, K_2/α is given by the difference between two large and almost equal numbers; hence a comparatively small error in their determination will produce a large percentage error in K_2/α . The largest percentage error in $[F^-]_T/[Fe^{+3}]_T$ also occurs in this region.

In Table 1 the values of K_1 and K_2 determined at different acidities are summarized. The value of K_2 given is the average of the values enclosed between the underscores in column 8, Tables 2 to 7. There seems to be a trend with $[H^+]$ concentration. It could be accounted for by the behavior of activity coefficients in mixed electrolytes,¹³ but most of the variation could be removed by using the smaller value of K_H given by Lamb and Jacques.¹⁰ When all the values are averaged, $K_1 = 188.5$ and $K_2 = 10.35$. By extrapolating to zero $HClO_4$ concentration the values $K_1 = 194$ and $K_2 = 10.7$ are obtained.

In Tables 3 and 4 the last four or five values of K_2/α show an increase of about 20 per cent, which is outside the experimental error. This increase is probably due to the formation of FeF_3 ; hence the equilibrium

is becoming important.

From the stoichiometric relation for iron and equilibria 1 and 2 the following equation can be derived:

$$\frac{[Fe^{+3}]_T}{[Fe^{+3}]} - \frac{K_H}{[H^+]} = 1 + K_1 \frac{[HF]}{[H^+]} + K_1 K_2 \frac{[HF]}{[H^+]} \quad (26)$$

In Fig. 4 a graph of $\log \left\{ \frac{[Fe^{+3}]_T}{[Fe^{+3}]} - \frac{K_H}{[H^+]} \right\}$ against $\log \frac{[HF]}{[H^+]}$ is given.

The solid curve was drawn using $K_1 = 188.5$ and $K_2 = 10.35$ in Eq. 26. Considering equilibrium 25, an equation analogous to Eq. 26,

$$\frac{[\text{Fe}^{+3}]_T}{[\text{Fe}^{+3}]} - \frac{K_H}{[\text{H}^+]} = 1 + K_1 \frac{[\text{HF}]}{[\text{H}^+]} + K_1 K_2 \frac{[\text{HF}]^2}{[\text{H}^+]^2} + K_1 K_2 K_3 \frac{[\text{HF}]^3}{[\text{H}^+]^3} \quad (27)$$

can be derived. By fitting Eq. 27 to the points which deviate at the upper end of the solid curve in Fig. 4, a value of $K_3 = 0.58$ was obtained. The dashed curve in Fig. 4 was drawn from Eq. 27 using $K_1 = 188.5$; $K_2 = 10.35$; $K_3 = 0.58$.

In analyzing the experimental data it has been assumed that the complexes FeF^{++} , FeF_2^+ , and FeF_3 exist. In the introduction good evidence for the existence of FeF_3 was presented. By inspection of some of the initial points in Tables 2 to 7 it is observed that the total iron complexed, $(\text{Fe}^{+3})_C$, is greater than one-half the total fluoride added; from this it can be concluded that FeF^{++} must be present. This leaves the possibility of fitting the data by assuming that only the two complexes FeF^{++} and FeF_3 are present in the solution. Equations similar to those used in the earlier part of this section were developed, and it was found that K_3 varied from $-20,000$ to $+4$ when K_1 was equal to 460. This variation could not be corrected by a change in K_1 .

Peters¹ studied the electrical conductivity and freezing points of separate solutions of FeCl_2 and NaF and of the combined solutions. He concluded that FeF_2 was essentially as dissociated as FeCl_2 . The activity coefficients of FeCl_2 indicate that it is completely dissociated.¹³ Even when allowance is made for a reasonable amount of experimental error in Peters's measurements, it can still be demonstrated that the complexing of Fe^{++} was not important in the experiments reported here. By allowing for a reasonable experimental error in Peters's freezing-point data and by considering an equilibrium of the type

$K' < 30$ is obtained. Since the experiments reported in this paper were performed in acid solution, the equilibrium must be written

Introducing the acid constant of HF, $K < 0.013$. In the experiments reported here the maximum value of $\frac{[\text{HF}]}{[\text{H}^+]}$ was about 0.5; hence

$\frac{[\text{FeF}^+]}{[\text{Fe}^{++}]} < 0.006$. In view of this result it is felt that there is justification for the conclusion that the complexing of ferrous ion was not important in these experiments.

4. ANALYSIS OF THE DATA FOR THORIUM

Since the equilibrium constants for equilibria 1 and 2 are known, the following quantities can be calculated for the cells with thorium: $[\text{HF}]/[\text{H}^+]$; $[\text{HF}] + [\text{F}^-] + [\text{HF}_2^-] = [\text{HF}]\alpha$; and $[\text{F}^-]_{\text{Fe}} = [\text{FeF}^{++}] + 2[\text{FeF}_2^+]$, the total fluoride complexed by ferric iron. The total fluoride complexed by thorium is then given by

$$[\text{F}^-]_{\text{Th}} = [\text{F}^-]_{\text{T}} - [\text{HF}]\alpha - [\text{F}^-]_{\text{Fe}} \quad (28)$$

The quantity $[\text{HF}]/[\text{H}^+]$ was calculated by solving the equation

$$\frac{[\text{Fe}^{+3}]_{\text{C}}}{[\text{Fe}^{+3}]} = K_1 \frac{[\text{HF}]}{[\text{H}^+]} + K_1 K_2 \frac{[\text{HF}]^2}{[\text{H}^+]^2} \quad (29)$$

after $[\text{Fe}^{+3}]_{\text{C}}/[\text{Fe}^{+3}]$ had been calculated from the observed change in potential and Eqs. 9, 10, and 14. Since all the experiments with thorium were carried out in approximately 0.05M HClO_4 , $K_1 = 191$ and $K_2 = 10.6$ were used in Eq. 29; these are the average values of K_1 and K_2 given in Tables 3 and 4. The term $K_1 K_2 K_3 \frac{[\text{HF}]^3}{[\text{H}^+]^3}$ which should have been included

in Eq. 29 was neglected because $[\text{HF}]/[\text{H}^+]$ was never large enough for an appreciable amount of FeF_3 to be formed. The values of $[\text{HF}]/[\text{H}^+]$ are given in column 3, Tables 8 to 11.

The equation for calculating $[\text{HF}]\alpha$ can be obtained by solving $[\text{H}^+]_0 = [\text{H}^+] + [\text{HF}]$ for $[\text{HF}]$ and is

$$[\text{HF}]\alpha = \frac{[\text{H}^+]_0 \alpha}{1 + \frac{[\text{H}^+]}{[\text{HF}]}} \quad (30)$$

The definition of α is given in Sec. 3.

From $[\text{F}^-]_{\text{Fe}} = [\text{FeF}^{++}] + 2[\text{FeF}_2^+]$ the following equation for $[\text{F}^-]_{\text{Fe}}$ is derived:

$$[\text{F}^-]_{\text{Fe}} = [\text{Fe}^{+3}]_{\text{C}} + K_1 K_2 [\text{Fe}^{+3}] \frac{[\text{HF}]^2}{[\text{H}^+]^2} \quad (31)$$

Substituting $[\text{HF}]\alpha$ and $[\text{F}^-]_{\text{Fe}}$ into Eq. 28 the values of $[\text{F}^-]_{\text{Th}}$ given in column 4, Tables 8 to 11, are calculated.

In column 5, Tables 8 to 11, $[F^-]_{Th}/[Th^{+4}]_T$, the total fluoride complexed by the thorium divided by the total thorium concentration, is tabulated. In Fig. 5 $[F^-]_{Th}/[Th^{+4}]_T$ is plotted against $\log \frac{[HF]}{[H^+]}$.

Several qualitative features of the curve should be noted. The abrupt breaks in the curve represent the points at which the solution has become saturated with respect to $ThF_4 \cdot 4H_2O$. These points shift with the total thorium concentration as they should, since the solubility product of thorium fluoride is volume dependent. The average number of fluorides per thorium rises above 2, indicating that a complex ion ThF_3^+ is present. Finally the points for different total thorium concentrations where no solid is present fall on the same curve as they should since the equilibria which determine the shape of this curve are not volume dependent. The scattering of points below $[F^-]_{Th}/[Th^{+4}]_T = 1$ is due to the fact that the equilibrium constant for the formation of ThF^{+3} is so much greater than that for the formation of FeF^{++} that almost no potential change is observed until about 1 fluoride per thorium has been added to the cell.

Assuming the equilibria

then

$$[F^-]_{Th} = [ThF^{+3}] + 2[ThF_2^{++}] + 3[ThF_3^+] \quad (35)$$

and when K'_1 , K'_2 , and K'_3 are introduced

$$[F^-]_{Th} = [Th^{+4}] \left\{ K'_1 \frac{[HF]}{[H^+]} + 2K'_1 K'_2 \frac{[HF]^2}{[H^+]^2} + 3K'_1 K'_2 K'_3 \frac{[HF]^3}{[H^+]^3} \right\} \quad (36)$$

From the stoichiometric relation for thorium and equilibria 32, 33, and 34

$$[Th^{+4}]_T = [Th^{+4}] \left\{ 1 + K'_1 \frac{[HF]}{[H^+]} + K'_1 K'_2 \frac{[HF]^2}{[H^+]^2} + K'_1 K'_2 K'_3 \frac{[HF]^3}{[H^+]^3} \right\} \quad (37)$$

In deriving Eq. 37 it was assumed that the degree of hydrolysis of the thorium is negligible in a 0.05M HClO_4 solution. This is indicated by the fact that a 0.24M $\text{Th}(\text{NO}_3)_4$ solution shows a pH of 2.4 on a Beckman pH meter.

Dividing Eq. 36 by 37

$$\frac{[\text{F}^-]_{\text{Th}}}{[\text{Th}^{+4}]_{\text{T}}} = \frac{\left\{ K'_1 \frac{[\text{HF}]}{[\text{H}^+]} + 2K'_1 K'_2 \frac{[\text{HF}]^2}{[\text{H}^+]^2} + 3K'_1 K'_2 K'_3 \frac{[\text{HF}]^3}{[\text{H}^+]^3} \right\}}{\left\{ 1 + K'_1 \frac{[\text{HF}]}{[\text{H}^+]} + K'_1 K'_2 \frac{[\text{HF}]^2}{[\text{H}^+]^2} + K'_1 K'_2 K'_3 \frac{[\text{HF}]^3}{[\text{H}^+]^3} \right\}} \quad (38)$$

Equation 38 was made to fit the data plotted in Fig. 5 by taking three points and solving the equations simultaneously for K'_1 , K'_2 , and K'_3 . The values obtained were $K'_1 = 4.5 \times 10^4$, $K'_2 = 649$, and $K'_3 = 31.6$. The curve drawn through the experimental points in Fig. 5 is a graph of Eq. 38 using the above values of the K 's. By picking different points and solving simultaneously, the values $K'_1 = 3.80 \times 10^4$, $K'_2 = 659$, and $K'_3 = 30.6$ were found. The curve drawn from these K values did not fit the experimental points at the lower end of the curve. The final values of the K 's were $K'_1 = 4.5 \pm 0.5 \times 10^4$, $K'_2 = 650 \pm 15$, and $K'_3 = 32 \pm 2$.

An attempt was made to fit the experimental curve using combinations of the equilibria 32, 33, and 34 two at a time, but it could not be done.

After the break has occurred in the curve, it is necessary to consider the equilibrium between the solid thorium fluoride and the complex ions in solution. It has been shown that the thorium fluoride precipitate obtained under the conditions of this experiment is $\text{ThF}_4 \cdot 4\text{H}_2\text{O}$ (reference 6); hence the solubility product is defined by the equilibrium

The ion ThF_2^{++} was used in defining the solubility product because it is the predominant species at the point of precipitation. When the solid is present, the stoichiometric relations for fluoride and thorium become

$$[\text{F}^-]_{\text{Th}} = [\text{ThF}^{+3}] + 2[\text{ThF}_2^{++}] + 3[\text{ThF}_3^+] + 4[\text{ThF}_4] \quad (40)$$

and

$$[\text{Th}^{+4}]_T = [\text{Th}^{+4}] + [\text{ThF}^{+3}] + [\text{ThF}_2^{++}] + [\text{ThF}_3^{+3}] + [\text{ThF}_4] \quad (41)$$

Multiplying Eq. 41 by 4, subtracting Eq. 40 from it, and introducing equilibria 32, 33, and 34

$$[\text{ThF}_2^{++}] = \frac{4[\text{Th}^{+4}]_T - [\text{F}^-]_{\text{Th}}}{\left[\frac{4}{K'_1 K'_2} \frac{[\text{H}^+]^2}{[\text{HF}]^2} + \frac{3}{K'_2} \frac{[\text{H}^+]}{[\text{HF}]} + 2 + K'_3 \frac{[\text{HF}]}{[\text{H}^+]} \right]} \quad (42)$$

Using the values of K'_1 , K'_2 , and K'_3 given above, the concentrations of $[\text{ThF}_2^{++}]$ given in column 6, Tables 8 to 10, were calculated employing Eq. 42. The solubility product is given in column 7, Tables 8 to 10. It should be noted that the average value of K_s increases by about 9 per cent in going from the experiment with the highest thorium concentration to the one with the lowest thorium concentration. This may be due to the fact that the initial ionic strength was inadvertently allowed to decrease in the same direction. However, this explanation does not seem very sound because the points where no solid is present do not show any such trend. The probable explanation is that the trend is caused by some unknown systematic error. The best value is taken as $K_s = 5.9 \pm 0.4 \times 10^{-8}$.

In Fig. 5 the curves drawn through the precipitation points were calculated using the individual averages for K_s . The equation for the curve may be obtained immediately from Eq. 42 and is

$$\frac{[\text{F}^-]_{\text{Th}}}{[\text{Th}^{+4}]_T} = 4 - \left[\frac{4}{K'_1 K'_2} \frac{[\text{H}^+]^2}{[\text{HF}]^2} + \frac{3}{K'_2} \frac{[\text{H}^+]}{[\text{HF}]} + 2 + K'_3 \frac{[\text{HF}]}{[\text{H}^+]} \right] \frac{K_s [\text{H}^+]^2}{[\text{Th}^{+4}]_T [\text{HF}]^2} \quad (43)$$

In summary the equilibria assumed and the equilibrium constants determined for them at 25°C and an ionic strength of 0.5 are given in Table 12.

5. ANALYSIS FOR THORIUM BY FLUORIDE PRECIPITATION

The cells described in the experimental section may be used for analysis for thorium. By carrying out titrations beyond the point where 4 fluorides per thorium had been added, it was found that the maximum in a graph of $\Delta E/\Delta \text{cc vs. cc}$ of NaF corresponded to 4 fluorides per thorium. In two titrations the observed volumes of NaF were 34.45 and 19.3 whereas the theoretical volumes for 4 fluorides per thorium were 34.32 and 19.35, respectively.

An objection to this type of titration as an analytical procedure for thorium is that 5 min is required between successive additions of

NaF solution; this would make a titration on an unknown solution require from $\frac{1}{2}$ to 2 hr, depending on the accuracy required. The time required for titration can be shortened by observing the point at which precipitation of thorium fluoride begins. Precipitation occurs when approximately 2 fluorides per thorium have been added to the solution; hence an estimate of the volume of NaF required for a sample may be made rapidly. Using this procedure it would be possible to determine the thorium concentration in a sample in less than $\frac{1}{2}$ hr and with an accuracy of well under 1 per cent.

Naturally this procedure cannot be used when rare earths, aluminum, scandium, zirconium, or other substances which react with fluoride are present.

Table 1—Summary of Results on Iron Fluoride Measurements

μ_0	$\frac{[\text{Fe}^{+3}]_T}{[\text{Fe}^{++}]_T}$	$[\text{H}^+]_0$	K_1	K_2	Table
0.52	0.576	0.0325	193	10.6	2
0.49	0.576	0.0533	190	10.6	3
0.53	2.42	0.0536	192	10.6	4
0.50	0.576	0.1110	187	10.2	5
0.51	2.42	0.1119	187	10.5	6
0.52	2.42	0.2781	182	9.62	7
Av.			188.5	10.35	

Table 2—Results of 0.0325M Acid*

($K_1 = 193$; $K_2 = 10.6$; $K_1/\alpha = 190$)

0.3675M NaF, cc	ΔE , mv	$\frac{[\text{Fe}^{+3}]}{[\text{Fe}^{++}]_T}$	$\frac{[\text{Fe}^{+3}]_C}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{F}^-]_T}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{HF}]_C}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{H}^+]}{[\text{Fe}^{+3}]_T}$	$\frac{K_2}{\alpha}$	α
0.101	12.40	0.5838	0.3830	0.556	0.160	49.5	21	1.013
0.203	25.67	0.3577	0.6320	1.118	0.433	49.2	6.5	1.013
0.304	37.96	0.2158	0.7719	1.674	0.790	48.8	10.2	1.014
0.406	48.80	0.1416	0.8504	2.236	1.209	48.4	10.7	1.014
0.506	57.61	0.1004	0.8939	2.787	1.655	48.0	10.4	1.014
0.606	65.55	0.0737	0.9221	3.338	2.121	47.5	10.6	1.014

*Initial conditions: $[\text{NaClO}_4] = 0.490\text{M}$; $[\text{HClO}_4]_0 = 0.03245\text{M}$; $[\text{Fe}^{+3}]_T = 0.0006539\text{M}$; $[\text{Fe}^{++}]_0 = 0.00136\text{M}$.

Table 3—Results at 0.0533M Acid*

 $(K_1 = 190; K_2 = 10.6; K_1/\alpha = 188)$

0.3675M NaF, cc	ΔE , mv	$\frac{[Fe^{+3}]}{[Fe^{+3}]_T}$	$\frac{[Fe^{+3}]_C}{[Fe^{+3}]_T}$	$\frac{[F^-]_T}{[Fe^{+3}]_T}$	$\frac{[HF]\alpha}{[Fe^{+3}]_T}$	$\frac{[H^+]}{[Fe^{+3}]_T}$	$\frac{K_2}{\alpha}$	α
0.101	10.50	0.6200	0.3356	0.557	0.212	81.3	39	1.008
0.162	16.86	0.5012	0.4813	0.893	0.389	81.1	13.6	1.008
0.223	22.93	0.3957	0.5905	1.229	0.596	80.9	10.5	1.008
0.284	28.86	0.3141	0.6749	1.565	0.825	80.7	<u>11.6</u>	1.008
0.345	34.08	0.2563	0.7347	1.901	1.076	80.4	10.4	1.008
0.406	39.00	0.2116	0.7810	2.238	1.341	80.2	10.3	1.008
0.506	46.24	0.1596	0.8348	2.789	1.795	79.7	10.4	1.009
0.606	52.65	0.1243	0.8713	3.340	2.263	79.2	10.7	1.009
0.806	63.51	0.08148	0.9157	4.442	3.248	78.3	10.6	1.009
1.004	72.47	0.05749	0.9405	5.535	4.250	77.3	10.6	1.010
1.305	83.73	0.03708	0.9616	7.19	5.800	75.7	10.5	1.010
1.705	96.35	0.02269	0.9765	9.40	7.904	73.6	<u>10.5</u>	1.012
2.208	110.06	0.01330	0.9862	12.16	10.57	70.9	11.0	1.013
2.812	123.67	0.00783	0.9919	15.50	13.85	67.7	11.2	1.015
3.815	142.93	0.00370	0.9962	21.02	19.26	62.2	11.7	1.019
5.015	162.33	0.00174	0.9982	27.62	25.79	55.7	12.1	1.024

*Initial conditions: $[NaClO_4] = 0.440M$; $[HClO_4]_0 = 0.05328M$; $[Fe^{+3}]_T = 0.0006539M$; $[Fe^{++}]_0 = 0.001136M$.

Table 4—Results at 0.536M Acid*

(K₁ = 192; K₂ = 10.6; K₁/α = 190)

0.3675M NaF, cc	ΔE, mv	$\frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{Fe}^{+3}]_C}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{F}^-]_T}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{HF}]\alpha}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{H}^+]}{[\text{Fe}^{+3}]_T}$	$\frac{K_2}{\alpha}$	α
0.061	6.91	0.739	0.2355	0.357	0.118	86.0	173	1.008
0.122	13.30	0.576	0.4040	0.714	0.295	85.9	22	1.008
0.183	19.81	0.4472	0.5373	1.070	0.502	85.7	13.5	1.008
0.243	25.81	0.3540	0.6338	1.421	0.735	85.4	11.1	1.008
0.304	31.46	0.2840	0.7061	1.778	0.994	85.2	10.4	1.008
0.406	39.88	0.2046	0.7883	2.374	1.465	84.7	10.0	1.008
0.506	47.12	0.1544	0.8403	2.960	1.956	84.2	10.0	1.009
0.706	59.35	0.09585	0.9008	4.130	2.983	83.2	10.6	1.009
0.905	69.17	0.06540	0.9323	5.29	4.04	82.1	10.7	1.009
1.205	81.24	0.04090	0.9677	7.05	5.67	80.5	10.9	1.010
1.605	94.57	0.02432	0.9748	9.39	7.92	78.2	10.7	1.011
2.107	108.77	0.01399	0.9855	12.32	10.74	75.4	11.2	1.013
2.711	123.00	0.00804	0.9917	15.85	14.19	72.0	11.6	1.015
3.416	137.18	0.00463	0.9952	19.97	18.24	67.9	11.9	1.017
4.115	149.64	0.00285	0.9971	24.08	22.30	63.9	12.2	1.020
5.015	164.08	0.00163	0.9983	29.33	27.50	58.7	12.6	1.024

*Initial conditions: [NaClO₄] = 0.478M; [HClO₄]₀ = 0.05359M; [Fe³⁺]_T = 0.0006220M; [Fe³⁺]₀ = 0.000257M.

Table 5—Results at 0.111M Acid*

(K₁ = 187; K₂ = 10.2; K₁/α = 186)

0.3675M NaF, cc	ΔE, mv	$\frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{Fe}^{+3}]_C}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{F}^-]_T}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{HF}]\alpha}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{H}^+]}{[\text{Fe}^{+3}]_T}$	$\frac{K_2}{\alpha}$	α
0.041	3.08	0.8725	0.1130	0.226	0.112	169.7	84	1.004
0.081	6.09	0.7762	0.2111	0.446	0.232	169.6	50	1.004
0.122	8.95	0.6945	0.2942	0.672	0.372	169.4	18	1.004
0.203	14.59	0.5554	0.4334	1.118	0.669	169.1	15.3	1.004
0.406	26.77	0.3468	0.6474	2.237	1.536	168.3	11.0	1.004
0.606	36.46	0.2379	0.7582	3.340	2.483	167.3	10.2	1.004
0.806	44.55	0.1736	0.8235	4.442	3.475	166.3	10.5	1.005
1.105	54.33	0.1186	0.8794	6.09	5.00	164.8	10.3	1.005
1.406	62.48	0.0864	0.9122	7.75	6.58	163.2	10.1	1.005
1.805	71.54	0.0607	0.9383	9.95	8.68	161.1	10.1	1.005
2.308	81.19	0.0417	0.9576	12.71	11.35	158.5	10.1	1.006
2.913	91.12	0.0283	0.9712	16.05	14.71	155.1	10.0	1.007
3.615	101.10	0.0192	0.9805	19.92	18.40	151.4	10.4	1.007
4.315	109.69	0.0138	0.9860	23.78	22.20	147.6	10.4	1.008
5.015	117.28	0.0102	0.9896	27.62	25.99	143.8	10.4	1.009

*Initial conditions: [NaClO₄] = 0.398M; [HClO₄]₀ = 0.1110M; [Fe³⁺]_T = 0.0006539M; [Fe³⁺]₀ = 0.001136M.

Table 6—Results at 0.112M Acid*

(K₁ = 187; K₂ = 10.5; K₁/α = 186)

0.3675M NaF, cc	ΔE, mv	$\frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{Fe}^{+3}]_C}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{F}^-]_T}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{HF}]\alpha}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{H}^+]}{[\text{Fe}^{+3}]_T}$	$\frac{K_2}{\alpha}$	α
0.101	7.55	0.7335	0.2543	0.591	0.331	179.5	6	1.004
0.203	14.72	0.5530	0.4360	1.187	0.734	179.1	8.4	1.004
0.304	21.23	0.4307	0.5623	1.778	1.181	178.6	9.4	1.004
0.506	32.20	0.2810	0.7144	2.960	2.166	177.6	9.9	1.004
0.706	41.31	0.1970	0.7998	4.130	3.174	176.6	11.9	1.004
1.004	51.77	0.1310	0.8668	5.875	4.815	175.0	10.6	1.004
1.5006	65.41	0.07705	0.9216	8.815	7.604	172.2	10.3	1.004
2.111	78.32	0.04663	0.9526	12.35	11.01	168.8	10.4	1.004
2.913	91.92	0.02744	0.9721	17.05	15.60	164.2	10.6	1.004
3.815	104.24	0.01700	0.9827	22.32	20.78	159.0	10.5	1.005
5.015	118.18	0.00988	0.9900	29.32	27.69	152.1	10.7	1.005

*Initial conditions: [NaClO₄] = 0.398M; [HClO₄]₀ = 0.1119M; [Fe³⁺]_T = 0.0006220M; [Fe³⁺]₀ = 0.000257M.

Table 7—Results at 0.278M Acid*

(K₁ = 182; K₂ = 9.6; K₁/α = 181)

0.3675M NaF, cc	ΔE, mv	$\frac{[\text{Fe}^{+3}]}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{Fe}^{+3}]_C}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{F}^-]_T}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{HF}]\alpha}{[\text{Fe}^{+3}]_T}$	$\frac{[\text{H}^+]}{[\text{Fe}^{+3}]_T}$	$\frac{K_2}{\alpha}$	α
0.203	8.19	0.7200	0.2750	1.188	0.908	446.1	18	1.002
0.406	15.11	0.5515	0.4447	2.374	1.912	445.1	8.4	1.002
0.706	23.80	0.3932	0.6041	4.130	3.484	443.5	10.2	1.002
1.205	34.88	0.2566	0.7428	7.05	6.22	440.8	9.54	1.002
2.006	47.90	0.1540	0.8450	11.73	10.72	436.3	9.50	1.002
3.014	60.21	0.09525	0.9041	17.63	16.49	430.5	9.63	1.003
4.015	69.90	0.06535	0.9342	23.48	22.24	424.8	9.69	1.003
5.015	77.75	0.04812	0.9516	29.32	28.00	418.9	9.52	1.003

*Initial conditions: [NaClO₄] = 0.239M; [HClO₄]₀ = 0.2781M; [Fe³⁺]_T = 0.0006220M; [Fe³⁺]₀ = 0.000257M.

Table 8—Data at 0.0536M Acid and 0.00477M Thorium*

0.3675M NaF, cc	ΔE , mv	$\frac{[HF]}{[H^+]} \times 10^4$	$[F^-]_{Th} \times 10^4$	$\frac{[F^-]_{Th}}{[Th^{+4}]_T}$	$[ThF_2^{++}] \times 10^4$	$K_s \times 10^8$
0.406	0.19	0.40	14.70	0.308		
0.806	0.32	0.68	29.22	0.612		
1.205	0.70	1.49	43.60	0.914		
1.506	1.67	3.63	54.21	1.136		
1.805	3.82	8.64	64.35	1.348		
2.107	7.01	16.75	74.26	1.556		
2.409	11.91	31.06	83.61	1.752		
2.711	15.28	42.28	93.47	1.959	30.1	5.39
3.014	15.63	43.52	104.4	2.187	27.0	5.11
3.416	17.01	48.56	118.5	2.483	23.3	5.48
3.815	18.46	54.08	132.6	2.778	19.3	5.63
4.215	20.05	60.40	146.6	3.071	15.0	5.46
4.615	23.23	74.06	160.0	3.352	10.8	5.93
5.015	28.18	98.25	172.7	3.620	6.5	6.3

Av. 5.61

*Initial conditions: $[NaClO_4] = 0.478M$; $[HClO_4]_0 = 0.0536M$; $[Fe^{+3}]_T = 0.0006220M$; $[Fe^{++}]_0 = 0.000257M$; $[Th^{+4}]_T = Th(NO_3)_4 = 0.004773M$.

Table 9—Data at 0.0536M Acid and 0.0012M Thorium*

0.3675M NaF, cc	ΔE , mv	$\frac{[HF]}{[H^+]} \times 10^4$	$[F^-]_{Th} \times 10^4$	$\frac{[F^-]_{Th}}{[Th^{+4}]_T}$	$[ThF_2^{++}] \times 10^4$	$K_s \times 10^8$
0.101	0					
0.203	0.08	0.17	7.36	0.616		
0.304	0.47	0.99	10.89	0.912		
0.406	1.91	4.18	14.10	1.179		
0.506	4.41	10.01	16.88	1.411		
0.606	8.11	19.85	19.27	1.611		
0.706	13.06	34.72	21.25	1.777		
0.806	18.79	55.3	22.95	1.919		
0.905	25.13	82.9	64.29	2.031		
1.004	26.73	90.8	27.30	2.282	7.35	6.06
1.105	28.21	98.4	30.40	2.542	6.27	6.08
1.205	30.05	108.3	33.33	2.788	5.24	6.15
1.406	34.83	136.7	38.67	3.232	3.31	6.18
1.805	50.54	261.7	45.40	3.797	0.812	5.54
2.610	84.63	775	47.41	3.964	0.095	5.9
5.015	140.69	3058	45.30	3.762		

Av. 5.99

*Initial conditions: $[NaClO_4] = 0.478M$; $[HClO_4]_0 = 0.0536M$; $[Fe^{+3}]_T = 0.0006220M$; $[Fe^{++}]_0 = 0.000257M$; $[Th^{+4}]_T = Th(NO_3)_4 = 0.001196M$.

Table 10—Data at 0.0559M Acid and 0.000237M Thorium*

0.3675M NaF, cc	ΔE , mv	$\frac{[HF]}{[H^+]} \times 10^4$	$[F^-]_{Th} \times 10^4$	$\frac{[F^-]_{Th}}{[Th^{+4}]_T}$	$[ThF_2^{++}] \times 10^4$	$K_s \times 10^8$
0.041	0.25	0.52	1.39	0.587		
0.101	2.41	5.32	2.78	1.173		
0.203	9.74	24.38	3.95	1.667		
0.304	18.87	54.8	4.53	1.912		
0.406	27.53	94.7	4.94	2.086		
0.506	35.39	140.0	5.24	2.212		
0.606	42.33	188.5	5.53	2.333		
0.706	48.02	237.5	6.10	2.574	1.15	6.5
0.806	52.39	280.1	7.09	2.992	0.78	6.2
0.905	56.89	328.3	7.79	3.290	0.53	5.7
1.004	61.02	378.0	8.47	3.575	0.30	(4.4)
1.406	75.63	598	10.76	4.55?		

Av. 6.1

*Initial conditions: $[NaClO_4] = 0.473M$; $[HClO_4]_0 = 0.0559M$; $[Fe^{+3}]_T = 0.0006160M$; $[Fe^{++}]_0 = 0.0002545M$; $[Th^{+4}]_T = Th(NO_3)_4 = 0.0002369M$.

Table 11—Data at 0.0536M Acid and 0.000239M Thorium*

0.0735M NaF, cc	ΔE , mv	$\frac{[HF]}{[H^+]} \times 10^4$	$[F^-]_{Th} \times 10^4$	$\frac{[F^-]_{Th}}{[Th^{+4}]_T}$
0.101	0.04			
0.203	0.15	0.33	1.42	0.595
0.304	0.45	0.99	2.05	0.857
0.365	0.73	1.57	2.40	1.002
0.406	1.20	2.61	2.53	1.057
0.506	2.23	4.90	2.90	1.212
0.606	3.44	7.70	3.21	1.343
0.706	4.91	11.30	3.43	1.436
0.806	6.34	14.96	3.68	1.539
0.905	7.98	19.41	3.85	1.610
1.004	9.62	24.04	4.02	1.682
1.205	13.13	34.97	4.31	1.803
1.406	16.80	47.76	4.53	1.896
1.805	24.09	78.0	4.88	2.042
3.014	43.15	196.4	5.55	2.322
5.015	62.94	403	8.18	3.422

*Initial conditions: $[NaClO_4] = 0.478M$; $[HClO_4]_0 = 0.0536M$; $[Fe^{+3}]_T = 0.0006220M$; $[Fe^{++}]_0 = 0.000257M$; $[Th^{+4}]_T = Th(NO_3)_4 = 0.0002390M$.

Table 12

Equilibrium	K (25°C, $\mu = 0.5$)
$\text{Fe}^{+3} + \text{HF} \rightleftharpoons \text{FeF}^{++} + \text{H}^+$	189 ± 3
$\text{FeF}^{++} + \text{HF} \rightleftharpoons \text{FeF}_2^+ + \text{H}^+$	10.4 ± 0.3
$\text{FeF}_2^+ + \text{HF} \rightleftharpoons \text{FeF}_3 + \text{H}^+$	0.58 ± 0.06
$\text{Th}^{+4} + \text{HF} \rightleftharpoons \text{ThF}^{+3} + \text{H}^+$	$45,000 \pm 5000$
$\text{ThF}^{+3} + \text{HF} \rightleftharpoons \text{ThF}_2^{++} + \text{H}^+$	650 ± 15
$\text{ThF}_2^{++} + \text{HF} \rightleftharpoons \text{ThF}_3^+ + \text{H}^+$	32 ± 2
$(\text{ThF}_4 \cdot 4\text{H}_2\text{O})_s + 2\text{H}^+ \rightleftharpoons \text{ThF}_2^{++} + 2\text{H}^+ + 4\text{H}_2\text{O}$	$5.9 \pm 0.4 \times 10^{-8}$

Fig. 1 —Cell used for the electrometric titrations.

Fig. 2—Graph of the effect of acid concentration on the variation of ΔE with HF concentration (cells containing no thorium).

Fig. 3 —Graph of the effect of thorium concentration on the variation of ΔE with HF concentration (acid concentration, approximately 0.05).

Fig. 4 — Logarithm of $\left\{ \frac{[\text{Fe}^{+3}]_T}{[\text{Fe}^{+3}]} - \frac{K_H}{[\text{H}^+]} \right\}$ plotted against logarithm of $\frac{[\text{HF}]}{[\text{H}^+]}$.

Fig. 5—Logarithm of $\frac{[HF]}{[H^+]}$ plotted against $\frac{[F^-]_{Th}}{[Th^{+4}]_T}$.

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Paper 7.8

PREPARATION OF BINARY COMPOUNDS
OF THORIUM FROM THORIUM METAL

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[Editor's Note: Work done at Iowa State College. Based on Report CC-2935. Prepared for publication June 19, 1945.]

ABSTRACT

The reactions between thorium hydride and various gases to produce finely divided anhydrous thorium compounds have been found to go smoothly in the temperature range 250 to 350°C. Reactions with chlorine, hydrogen chloride, bromine, hydrogen bromide, hydrogen fluoride, hydrogen iodide, phosphine, hydrogen sulfide, and water have been carried out. No reaction was observed with methane or carbon dioxide.

1. INTRODUCTION

As recently as 1937¹ a patent was issued for the preparation of thorium halides by passing a halogen over thoria intimately mixed with carbon. The reaction was carried out at very high temperatures, 600 to 900°C in quartz chambers, and the pure halide was obtained by sublimation from the crude. This is a classical method employed long ago by Berzelius.

The recent availability of relatively pure thorium metal has made possible the production of many thorium salts from the metal via the hydride just as has been done in the case of uranium and the rare earths.²

If a piece of thorium metal is converted to the hydride, then the reaction can be carried out with the hydride, or the hydride can be decomposed and the powdery metal allowed to react, or there may be a

combination of the two. In any event the purity of the final product will depend upon the purity of the metal employed. The greatest impurity in the thorium cast at Ames is ThO_2 (about 0.5 per cent). By using this relatively pure metal in making compounds, the need for any further treatment of the salt, such as sublimation or extraction, is eliminated.

At the time of writing, experiments show the existence of two hydrides,²⁵ but, since this does not appear to influence the reactions to be described below, ThH_4 will be used to represent the intermediary stage. The identities of the product compounds were established by x-ray and/or chemical analysis.

2. EXPERIMENTAL WORK

2.1 General Experimental Method. The thorium metal sample was soaked in carbon tetrachloride to remove all oil, then rinsed in ether, and finally dried in vacuum. It was found that washing the metal with dilute hydrochloric acid did not improve the hydride formation. The cleaned piece of metal was enclosed in 25-mm glass tubing 20 cm long. Both ends of the chamber were plugged with glass wool, drawn down to 9 mm, and sealed to a three-way stopcock. The chamber was heated by a resistance furnace. After it was set up, the system was thoroughly flushed with hydrogen at room temperature, and the temperature was raised to 350 to 400°C for the hydride formation. The hydride was best obtained in a powder form by cooling the system and bringing it back up to 400°C repeatedly, shaking the chamber at the same time. After the hydride was completely pulverized, the flow of hydrogen was continued for a short time, and this was followed by the reagent gas at the desired temperature. When the reaction was thought complete, the system was allowed to cool in the atmosphere of the reagent gas; when the temperature of the system fell below 100°C, it was flushed with nitrogen.

2.2 Reaction of HCl and Cl_2 with Thorium Hydride. Berzelius prepared thorium chloride³ by the action of chlorine on ThO_2 and carbon at 750°C; Smith and Harris⁴ by the action of PCl_5 on ThO_2 ; Kruss and Nilson⁵ by passing HCl over Th at red heat; Matignon⁶ by passing Cl_2 - S_2Cl_2 over ThO_2 and by passing CCl_4 over ThO_2 ; and Moissan⁷ by passing Cl_2 over ThC_2 . All these methods were run at high temperature and depended upon sublimation of ThCl_4 at 850°C for purity. Rosenheim et al.⁸ prepared the hydrated chloride from the fractional crystallization of ThO_2 in alcoholic hydrochloric acid. Ephraim⁹ recommends the direct action of Cl_2 on Th, subliming the chloride away as it is formed.

In the method described here, HCl was passed over the hydride at 350°C for 3 hr. When the reaction appeared complete, the HCl was turned off, and the system was allowed to cool in an atmosphere of helium (although it could have been allowed to cool in an atmosphere of HCl and then flushed by any inert gas). A greyish-white product resulted.

From the 16.40 g of Th taken, 25.87 g of ThCl₄ was produced, which is 97.88 per cent of the theoretical for ThCl₄. Chemical analysis showed that 98.08 per cent went into solution in H₂O to give ThCl_{3.92}. The insoluble material was identified as thorium dioxide.

The x-ray pattern was compared visually with the pattern of uranium tetrachloride, with which thorium chloride is isomorphous. Maxima were checked and no extra maxima were observed. The reaction can be represented by the following equation:

In the reaction with chlorine, the chlorine was diluted to 1 part in 10 of helium and was allowed to pass over the hydride at a slow rate. The reaction went slowly at 250°C but rapidly at 400°C. The final product was greyish-white, soluble in water with a hiss, and very hygroscopic. The equation for the reaction is

If the chlorine is not diluted the reaction goes very vigorously, causing the reaction chamber to glow and producing pellets of hydride covered with molten chloride which prevents the reaction from going to completion. No analysis was made on this chloride.

2.3 Reaction of HBr and Br₂ with Thorium Hydride. The methods in the literature for preparing thorium bromide are similar to those already given for the chloride. Bourion¹⁰ prepared it by the action of S₂Cl₂ and HBr on ThO₂ at 135°C; Young and Fletcher¹¹ prepared it by the action of Br₂ with N₂ as a carrier on ThO₂ + C at 800 to 900°C. It can be made by direct synthesis from the elements.¹²

The method used at Ames was carried out as follows: Hydrogen bromide was generated by bubbling hydrogen through bromine, and the gases were allowed to pass through platinized asbestos heated to 400°C. The reaction of the HBr on the hydride proceeded smoothly at 350°C, at which temperature an even flow of the gas was maintained for 4 hr. The system was cooled and the product was weighed.

From the 10.945 g of Th used, 25.90 g of ThBr₄ was produced; the theoretical value for ThBr₄ is 26.042 g. Conversion was 92.4 per

cent complete; 0.768 g did not go into solution. The dissolved portion (93 per cent) analyzed to give a Br/Th ratio of 3.39.

In the bromine reaction, the bromine was carried by nitrogen. The optimum temperature for this reaction was around 400°C; it gave a product which was greyish white and analyzed to give a Br/Th ratio of 3.39.

2.4 Reaction of HF with Thorium Hydride. Thorium fluoride has been prepared¹³ by the action of HF on ThO₂ and of PbF₂ or HgF₂ on ThO₂. Berzelius obtained the hydrate by the action of HF solution on ThO₂.³ Chydenius¹⁴ obtained the same by adding the acid to ThCl₄, and Chauvenet¹⁵ obtained the hydrate from Th(NO₃)₄ and AgF solutions. Moissan⁷ prepared the anhydrous fluoride by the action of fluorine on ThCl₄, Chauvenet¹⁵ prepared it by passing HF over ThCl₄ and ThBr₄, and Duboin¹⁶ did the same by melting KThF₅ with an excess of KCl. In the preparation described here, HF was passed over the hydride at 350°C for 2 hr in a nickel apparatus. The action with fluorine was not tried.

From the 24.80 g of Th taken, 32.90 g of ThF₄ was produced; the theoretical value for ThF₄ is 32.95 g. The analysis shows a complete conversion, giving a F/Th ratio of 4.0.

The preparation of thorium fluoride is represented by the equation

2.5 Reaction of HI with Thorium Hydride. Thorium iodide has been prepared by the action of any one of the following: HI, SiI₄, Cl₄, BI₃, PI₃, or S₂I₂ (+I₂) on ThO₂ (reference 17), by the action of I₂ vapor¹⁸ on Th; the hydrate has been obtained by extraction of the mother liquor resulting from the reaction of alcoholic hydriodic acid on thoria.⁸

The preparation of the iodide at Ames is given by the following equation:

HI was generated by the action of P₂O₅ on hydriodic acid, and the HI was passed over the hydride at 350°C. The metal gained 86.59 per cent of the theoretical weight for ThI₄. The product was yellowish and gave an I/Th ratio of 3.67 on analysis.

2.6 Reaction of Phosphine with Thorium Hydride. Thorium phosphide has been made by direct combination of the elements, although Montignie²⁰ claims that he could not make it by direct combination, displacement, or by reduction of the phosphate. It has, however, been identified by Zumbusch²¹ and by Meisel.²²

Phosphine reacts with hydride according to the equation

Phosphine was generated by the action of strong potassium hydroxide solution on yellow phosphorus. The reaction chamber was maintained at 400°C while the phosphine passed over the hydride. The product had a dark steel-gray appearance and was virtually insoluble in all standard laboratory reagents.

X-ray analysis revealed a strong body-centered cubic structure with $a_0 = 8.624 \pm 0.02$ Å, which checks excellently with that found by Meisel²² for Th_3P_4 .

2.7 Reaction of H_2S with Thorium Hydride. ThS_2 was prepared by Berzelius³ by the action of S or H_2S over heated thorium, by Moissan and Etard²³ by the action of S over ThC_2 , and by Kruss and Volk²⁴ by the action of H_2S on ThCl_4 plus KCl_4 . Picon¹⁹ prepared ThS_2 by the action of H_2S on ThO_2 in a graphite crucible at 600°C. The colors for thorium sulfide have variously been described as yellow, black, and dark brown.

The hydride method of preparing sulfide is represented by the equation

Two experiments were carried out in preparing the sulfide. In one case H_2S was passed over the hydride at 300°C, and in the second case it was passed over at 400°C. In both cases, the gain in weight was that which would be given by conversion to ThS_2 . The sulfides were dark brown. X-ray analysis gave very weak Th lines, strong ThS_2 lines, and no other lines that could be identified in any of the other phases reported in the Th-S system by Meisel.²²

2.8 Reaction of Water and Thorium Hydride. The hydride was formed in the usual manner. The apparatus was so arranged that steam could generate directly into the chamber held at 100°C without condensing. The initial 12.671 g of metal gave 12.884 g of hydride. After 6 hr, when 150 cc of H_2O had passed over, the product weighed 14.329 g. This is 99.38 per cent of the theoretical ThO_2 , indicating

that steam over hydride forms the oxide. The presence of oxide was confirmed by x-ray analysis. The equation for the reaction is

2.9 Reaction of CO_2 and Thorium Hydride. The hydride was formed in the usual manner. The initial 11.73 g of metal gave 11.90 g of hydride. Carbon dioxide was passed over the hydride at 350°C for 47 hr to give a product weighing 12.0 g. X-ray examination showed no carbide or oxide. Hence thorium hydride is stable in an atmosphere of carbon dioxide up to at least 350°C .

2.10 Reaction of Methane and Thorium Hydride. Methane gas was purified by passing it through a Vycor chamber containing uranium and uranium carbide heated to 900°C . The methane passed over the hydride for $21\frac{1}{2}$ hr at 500°C . The initial 6.8369 g of thorium gave 6.9430 g of hydride. The final product weighed 6.8868 g, thus losing from the hydride. X-ray examination showed the product to be principally a subhydride of the composition ThH_2 . Thus a dehydrogenation of ThH_4 took place in an atmosphere of CH_4 at 500°C .

3. CONCLUSION

Thorium hydride, or the powdery metal obtained from the decomposition of the hydride, has been shown to be very useful in preparing anhydrous thorium salts by its reaction with various gases.

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Paper 7.9

PRECIPITATION OF THORIUM OXALATE FROM NITRIC ACID SOLUTIONS

By A. S. Ayers

[Editor's Note: Work done at Iowa State College. Based on Report CC-2962. Prepared for publication Oct. 5, 1945.]

1. INTRODUCTION

It has been known for a long time that thorium is precipitated by oxalic acid in acid solutions, but a survey of the literature showed no study of the limits of the acidity and oxalic acid excess which yield quantitative results. Spitzin reports on the solubility of thorium oxalate in varying concentrations of several acids,¹ but the effect of an excess oxalic acid is not included. Since solutions presented for analysis sometimes contain more than the recommended 2 per cent mineral acid,² it would be advantageous to be able to remove quantitatively the thorium without otherwise altering the solutions. This was especially of interest in solutions containing bismuth, since it was hoped that small amounts of thorium could be precipitated in nitric acid solutions containing large quantities of bismuth. In removing the bismuth first by a bismuth oxychloride precipitation, there is every opportunity for carrying of the thorium.

2. EXPERIMENTAL WORK

Standard solutions of thorium nitrate were made from reagent-grade thorium nitrate and analyzed by evaporating aliquots to dryness and igniting in platinum. Aliquots of these solutions were acidified with known amounts of nitric acid, diluted to known volumes, and heated almost to boiling. A small amount of filter pulp was added, and a weighed amount of oxalic acid was introduced. The oxalic acid con-

centration was varied from the theoretical amount to six times that quantity (500 per cent excess). The nitric acid content ranged from 0.0N to 2.6N. The samples were allowed to cool to room temperature and then were filtered through Schleicher & Schüll Co. White Ribbon paper (or its equivalent). Some authors recommend allowing the thorium oxalate to stand for 10 to 12 hr,² but the use of filter pulp permits filtration after 1½ to 2 hr with accurate results. The precipitates were dried, charred at a low temperature, and then ignited in platinum in the muffle at 1000°C. Ignition at lower temperatures (700 to 800°C) produces an oxide that is slightly hygroscopic; higher temperatures prevent this. The results obtained are tabulated in Table 1.

3. CONCLUSIONS

Reproducible results were not obtained at oxalic acid concentrations higher than 0.45N in the solution after precipitation. It may well be noted here that the density of the precipitate depended upon the nitric acid concentration; at 1.5N to 1.8N nitric acid the moist precipitate occupied approximately one-half as much space on the filter as at 0.4N to 0.6N nitric acid. This is of importance in the handling of large quantities of thorium. The variation of the low-concentration nitric acid samples can be explained by noting that a soluble complex oxalate is formed from thorium oxalate in neutral or slightly acid solutions.

A graphic representation of the results is presented in Fig. 1; here normality of nitric acid is plotted against grams of thorium dioxide recovered, with a different curve for each value of the normality of the excess oxalic acid used.

4. RECOMMENDED PROCEDURE

An aliquot containing about 1.5 g of thorium (as metal) is taken for analysis since this is the maximum amount that can be handled readily in an analysis. This is diluted to a volume of 200 to 300 ml and heated to boiling. A small amount of macerated filter pulp is added, and the oxalic acid is stirred in as crystals. If the solution is 0.2N in HNO_3 , 100 per cent excess oxalic acid is adequate; 1.0N HNO_3 requires 200 per cent, and 1.8N requires 400 per cent excess. The solution is removed from the hot plate, allowed to cool to room temperature, and then filtered through a medium-speed ashless filter paper. The precipitate and paper are placed in a weighed platinum crucible, dried at 110°C, charred at 300°C, and ignited at 1000°C. The conversion factor of Th/ThO_2 is 0.8785.

Table 1 — Results of Oxalate Precipitations

HNO ₃ normality	Excess H ₂ C ₂ O ₄ , %	Normality of H ₂ C ₂ O ₄ in supernatant liquid	Recovery, %		
0.1*	0	0.000	99.45	99.80	99.90
0.2*	10	0.0058	99.80	99.75	99.50
0.3*	10	0.0058	99.70	99.50	99.45
0.4*	10	0.0058	99.70	99.50	99.75
0.1*	25	0.0145	99.85	99.80	100.10
0.3*	25	0.0145	100.00	99.95	99.75
0.4*	25	0.0145	99.50	99.50	
0.4*	50	0.029	99.50	99.40	99.75
0.6*	50	0.029	99.55	99.50	
0.4*	100	0.058	100.0	99.45	99.85
0.6*	100	0.058	100.20	100.15	99.90
0.2	125	0.125	99.85	100.00	
0.4	125	0.125	100.00	99.80	
0.6	125	0.125	99.30	99.80	
0.8	125	0.125	99.55	99.80	
1.0	125	0.125	99.45	99.85	
0.0	240	0.236	100.15		
0.2	240	0.236	100.10		
0.4	240	0.236	100.00	99.80	
0.6	240	0.236	99.85	100.10	
0.8	240	0.236	100.05	100.00	
1.0	240	0.236	100.05	100.00	
1.2	240	0.236	99.90		
1.4	240	0.236	99.55		
0.6	350	0.348	99.95		
0.8	350	0.348	100.05		
1.0	350	0.348	100.00		
1.2	350	0.348	99.95		
1.4	350	0.348	100.00		
1.6	350	0.348	99.80		
1.4	450	0.445	100.00		
1.6	450	0.445	99.90		
1.8	450	0.445	100.00		
2.0	450	0.445	99.30		
2.4	450	0.445	99.55		
2.4	450	0.445	98.30		

*These values are for samples of 0.7671 g of ThO₂, while the remainder are for 1.3046 g of ThO₂ per sample. All sample volumes were 200 ml.

Fig. 1 — Thorium recovery versus nitric acid normality at various oxalic acid concentrations.

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Paper 7.10

NOTE ON THE EFFECT OF HYDROCHLORIC ACID
CONCENTRATION ON THE HEAT OF SOLUTION
OF THORIUM TETRACHLORIDE

By E. F. Westrum, Jr., and H. P. Robinson

[Editor's Note: Contribution from the Argonne National Laboratory. Based on work reported in MUC-GTS-1808. Prepared for publication June 27, 1945.]

The need of checking certain calorimetric techniques¹ provided an opportunity to make heat-of-solution measurements on a very pure sample of anhydrous thorium tetrachloride which was sublimed in a quartz tube in high vacuum to eliminate any oxychloride present. About 50 per cent of the material was sublimed, sealed off, and loaded into the sample bulbs within a dry box. The analytical section analyzed this material as 62.8 per cent Th and 37.8 per cent Cl [analysis by B. Holt, reported by R. W. Bane, Report MUC-JIW-530, May 15, 1945] (theoretical, 62.07 per cent Th and 37.93 per cent Cl). Although the analysis totals more than 100 per cent and therefore cannot be regarded as proof of the absence of oxychloride, it is estimated that the presence of as much as 2 per cent of oxychloride would affect the heat of solution less than several tenths of 1 per cent.

As might be expected, the observed rate of change of the heat of solution with concentration of HCl is considerably larger than that of a trivalent ion of similar radius.²

The value of Chauvenet³ for the heat of formation of ThCl_4 is based upon heats of solution of Th in about 3.6M HCl and ThCl_4 in water (-56.7 Kcal/mole). Our data indicate that the neglect of the effect of the HCl concentration in the combination of these thermochemical data makes the value of Chauvenet for the heat of formation about 9 Kcal too

large. Similarly distorted values appear among many of the heats of formation of thorium compounds tabulated by Bichowsky and Rossini.⁴ A redetermination of the heat of formation of ThCl_4 is considered very desirable.

Table 1 — Heat of Solution of ThCl_4 in Hydrochloric Acid*

Molarity of HCl	Weight of acid (vacuo), g	ThCl_4 (vacuo), millimoles	Heat evolved, cal	Heat of solution Kcal/mole
1.000	192.25	0.7081	40.66	57.43
		0.8827	50.68	57.41
				57.42 ± 0.1
6.000	212.25	1.0258	45.30	44.16
		1.2323	54.54	44.27
				44.27 ± 0.1
9.000	217.25	1.4136	49.39	34.94
		1.4256	49.74	34.89
				34.93 ± 0.1

*Operating conditions: temperature, 25.0°C; molecular weight of ThCl_4 , 373.95.

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Editor's Note

The indexes for Parts 1 and 2 are combined and are included in Part 2.

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PRODUCTION AND SEPARATION OF U^{233}

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TID-5223 PART II

Paper 8.1

PRECIPITATION OF THORIUM OXALATE

By Henry Lipkind and A. S. Newton

[Editor's Note: Work done at Iowa State College. Based on Report CC-2395. Prepared for publication Feb. 19, 1945.]

ABSTRACT

The conditions necessary for the precipitation of thorium oxalate in a crystalline form which will filter well have been investigated. The effect of nitric acid, calcium nitrate, and methyl isobutyl ketone on the precipitation is discussed.

1. INTRODUCTION

The plans discussed here for the purification of thorium¹ involve the extraction of thorium nitrate with hexone, the re-extraction of the thorium nitrate from hexone to water, and the conversion of the thorium to the desired salt from the product solution.

If metal is to be produced, the thorium nitrate must be precipitated as some salt and converted to anhydrous thorium fluoride. A consideration of the properties of the possible salts for precipitation, i.e., fluoride, hydroxide, oxalate, and carbonate, all of which can be converted to anhydrous ThF_4 with HF , led to the conclusion that the oxalate was the most easily filtered (or centrifuged) precipitate of the above materials. Under suitable conditions thorium oxalate precipitates in a crystalline state which is easily filtered or centrifuged in a basket centrifuge and is thus easily washed. Under other conditions, the oxalate precipitates as an almost gelatinous precipitate which cannot be filtered well, leaving a wet slurry on the filter paper or in the centrifuge basket. As an example, a precipitate of thorium oxalate from a

solution 0.196M in thorium nitrate, 1M in HNO_3 , and saturated with hexone gave a precipitate which was impossible to filter to a dry cake, and much of the precipitate ran through the filter. The residue on the filter was a pasty mass which was difficult to handle.

Therefore it became necessary to investigate the conditions under which thorium oxalate could be thrown down as a crystalline precipitate if the oxalate was to be precipitated from the product from the purification columns. The procedure in all cases was as follows: The solution containing $\text{Th}(\text{NO}_3)_4$, $\text{Ca}(\text{NO}_3)_2$, and HNO_3 in various proportions was made up at room temperature, and the $\text{H}_2\text{C}_2\text{O}_4$ was added. Experiments showed that there was no difference in the results from adding the oxalic acid as the dihydrate crystals or as a warm saturated solution. A 5 per cent excess of oxalic acid was shown to be sufficient to precipitate all the thorium; consequently this excess was used in all experiments. In cases where the thorium nitrate was saturated with hexone or was heated, this was done before adding the oxalic acid.

The ease of filtration of the precipitate with suction on a Buechner funnel was taken as a criterion of desirability of the precipitate. The point of demarcation between desirable and undesirable precipitates was fairly sharp; thus minimum concentrations of each of the various components necessary to give a desirable precipitate could be readily determined.

2. EXPERIMENTAL WORK

2.1 Thorium Nitrate and Nitric Acid. The concentration of nitric acid was varied from 1N to 6N. The concentration of thorium was varied by stages from 0.1 g of $\text{Th}(\text{NO}_3)_4$ per cubic centimeter (0.184M Th^{+4}) to 0.5 g of $\text{Th}(\text{NO}_3)_4$ per cubic centimeter (0.919M Th^{+4}). The experiments were carried out at both 25 and 75°C. The results given in Table 1 represent the minimum concentration of constituents which will give a desirable precipitate of thorium oxalate as described previously.

No acidities of HNO_3 below 1N were investigated; thus at 75°C much lower acidities might give a desirable precipitate at concentrations of Th^{+4} greater than 0.5M.

2.2 Thorium Nitrate, Nitric Acid, and Methyl Isobutyl Ketone. The satisfactory conditions found in Table 1 were still found to be satisfactory when the solution was saturated with hexone before the oxalic acid was added. In no case did the ketone in any way affect the character of the oxalate precipitate, and in all cases the ketone was apparently washed out of the thorium oxalate with water. It was found

that, if the solution was heated to 80°C in the presence of hexone, the nitric acid reacts to form isobutyric acid (as evidenced by the odor). This could not be completely removed from the thorium oxalate by washing. However, in 6N HNO₃ at 75°C the rate of oxidation of the hexone was too slow to be noticeable, but this represents the safe upper limit of temperature that can be used without the formation of isobutyric acid.

2.3 Thorium Nitrate, Nitric Acid, and Calcium Nitrate. The effect of the presence of Ca(NO₃)₂ in the solution of Th(NO₃)₄ upon the precipitation of Th(C₂O₄)₂ was studied along two lines: (1) the concentration of calcium nitrate that is necessary to bring about the desired oxalate precipitate and (2) the amount of calcium that is carried down in this precipitate. The following concentrations were employed: 1M and 2M HNO₃, 0.184M and 0.368M Th⁺⁴, and Ca(NO₃)₂ from 0.1M up. The studies were made at 25 and 75°C. The results are as follows:

- (1) 1M HNO₃, 0.184M Th⁺⁴ at 25°C requires 0.3M Ca(NO₃)₂
- (2) 1M HNO₃, 0.368M Th⁺⁴ at 25°C requires 0.1M Ca(NO₃)₂
- (3) 2M HNO₃, 0.184M Th⁺⁴ at 25°C requires 0.2M Ca(NO₃)₂

These represent the minimum necessary concentrations for HNO₃, Th⁺⁴, and Ca⁺⁺ at 25°C. It was found that at 75°C the minimum concentration of Ca(NO₃)₂ which gave a good precipitate with 1M HNO₃ and 0.184M Th⁺⁴ was 0.1M Ca(NO₃)₂.

These experiments were carried out with mantle-grade thorium nitrate which contained 120 to 140 ppm of calcium. Sample 1 above had 2500 ppm of Ca in the precipitate, equal to 1.213 per cent of the amount of calcium added. Sample 3 contained 2000 ppm of Ca in the precipitate, equal to 1.358 per cent of the amount of calcium added.

In all experiments the oxalic acid was added as solid and as solution with no difference in the results. Again an excess of 5 per cent of oxalic acid proved enough to give quantitative precipitation of the thorium.

The study with added Ca(NO₃)₂ is summarized in Table 2, in which are given representative concentrations which yield a satisfactory precipitate of thorium oxalate.

3. DISCUSSION OF RESULTS

The studies tabulated above show that the character of the precipitate is controlled by the ionic strength of the solution. This may be somewhat controlled by (1) controlling the HNO₃ concentration in the feed to the column, (2) by changing the flow rate of the reextraction water to increase the HNO₃ and Th(NO₃)₄ concentration in the product solution, and (3) by adding HNO₃ or Ca(NO₃)₂ to the product solution

before adding the oxalic acid. With present plans for concentration and rates, the product solution should give a satisfactory precipitate of $\text{Th}(\text{C}_2\text{O}_4)_2$ at room temperature.

The presence of calcium oxalate in the thorium oxalate is not objectionable if it does not exceed a few per cent since calcium is used in the reduction and this will increase the amount of slag only slightly. Satisfactory reductions have previously been carried out with as much as 3 per cent Na in the ThF_4 , showing that inert materials (in this case, NaF) in the slag do not interfere in the reduction.

Table 1—Minimum Concentrations for Satisfactory Precipitation of Thorium Oxalate

Concentration of $\text{Th}(\text{NO}_3)_4$, g/cc	Concentration as Th^{+4} (molarity)	Normality of HNO_3 necessary to yield a desirable precipitate	
		At 25°C	At 75°C
0.1	0.184	6	6
0.2	0.368	6	2
0.3	0.514	4	1
0.4	0.737	2	1
0.5	0.919	1	1

Table 2—Representative Concentrations Which Yield a Satisfactory Precipitate of Thorium Oxalate in the Presence of Calcium Nitrate

Concentration of Th^{+4} (molarity)	Concentration of HNO_3 (molarity)	Concentration of $\text{Ca}(\text{NO}_3)_2$ (molarity)	Temperature, °C
0.184	1	0.3	25
0.184	1	0.2	70
0.184	2	0.1	25
0.368	1	0.1	25

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Paper 8.2

A METHOD OF RECOVERING THORIUM FROM SLAG MATERIALS

By Oliver Johnson and R. W. Fisher

[Editor's Note: Work done at Iowa State College. Based on Report CC-2401. Prepared for publication Mar. 23, 1945.]

ABSTRACT

A method of recovering thorium from slag from the bomb process of producing thorium has been developed. Hydrochloric acid and sodium hydroxide are the only chemicals required in quantity. Materials required for a representative slag are given.

1. INTRODUCTION

The slag from the reduction of thorium fluoride with calcium, using zinc chloride as a booster, contains the following substances: Ca, CaO, ThO₂, Fe, ZnF₂, CaF₂, Zn, Th, and unreduced ThF₄. It is desired to extract the thorium from this slag and precipitate it in a form suitable for reconversion to anhydrous thorium fluoride.

2. EXPERIMENTAL WORK

It has been found that a water leach serves to disintegrate the slag material very well. Since much heat is produced in the reaction, the slag is added to water. There is evolution of hydrogen and acetylene, and a thick slurry is formed. All the thorium remains in the solid phase. The filtrate which is saturated with calcium hydroxide can be discarded.

A treatment of the above residue by concentrated hydrochloric acid dissolves all free thorium metal, thorium hydroxide, iron, calcium oxide, and zinc salts. The insoluble material is calcium fluoride, thorium fluoride, and thorium oxide.

The filtrate is made 1N to 3N in hydrochloric acid, and thorium is precipitated by adding oxalic acid. Before this precipitation of thorium oxalate, a small amount of nitric acid is added to keep iron in ferric form and to prevent coprecipitation of ferrous oxalate. Complete precipitation of thorium oxalate requires 12 hr.

Several methods have been tested to recover the remaining thorium from the acid-insoluble residue. A sample of slag was digested with concentrated sulfuric acid for 5 hr, and the resulting slurry was poured into cold water. The filtrate contained only about 5 per cent of the total thorium in the residue.

Digestion of the acid-insoluble residue in 60 per cent perchloric acid proved to be very effective. Five grams of the residue dissolved in 10 ml of concentrated perchloric acid in 2 hr of heating. The cost and unavailability of large quantities of perchloric acid prohibit the use of this method on a recovery process, but it does constitute a convenient method of assaying slag for total thorium content.

Fusion with ammonium oxalate was studied as another possible method. The fusion must be carried out in a nickel or monel crucible at 550°C, and the weight of ammonium oxalate required is four times that of the slag. There is considerable frothing during the fusion. To dissolve the melt completely, it must be removed from the crucible and boiled with aqua regia in a pyrex beaker. Although the reagents required are not costly, the process is not readily adaptable to large-scale operations.

Digestion with ferric nitrate solution and ferric nitrate-nitric acid mixtures did not dissolve the slag residue.

Experiments using a metathesis reaction with a 50 per cent sodium hydroxide solution are the most promising of the methods. This process converts the thorium salts to the less soluble thorium hydroxide. After a 4-hr boiling, the thick slurry is diluted with water to about four times the volume and filtered. The residue, which still contains all the thorium, is extracted with 6N hydrochloric acid. A second treatment with sodium hydroxide can be carried out on the residue if assay shows it to contain much thorium. From a limited number of experiments it appears that one such treatment will be sufficient. This method is practicable because the sodium hydroxide treatment can be carried out in an iron vessel and the chemicals required are relatively inexpensive.

3. PROPOSED PROCESS FOR RECOVERY OF THORIUM FROM SLAG

The data given below are for a representative slag sample weighing 1 kg.

Step 1. Leach with 1 liter of water. Filter and discard the filtrate.

Step 2. Treat the residue from the water leach (1220 g when dried) with concentrated hydrochloric acid. Concentrated hydrochloric acid in the amount of 3300 ml or 7.32 lb is required. Filter—the filtrate contains thorium and is 1N to 3N in HCl. Add 10 ml concentrated nitric acid. Add a solution containing 70 g of oxalic acid (100 per cent excess) and let stand for 12 hr. Eighty-one grams of the oxalate (equivalent to 46.2 g of thorium) is produced.

Step 3. The acid-insoluble residue (230 g) is mixed well with 200 g of flake sodium hydroxide, and water is added to give a volume of approximately 400 ml. It is gently boiled for 4 hr. It is then diluted to 1 to 2 liters and filtered. The filtrate is discarded, and the residue is treated with 6N hydrochloric acid. The treatment is repeated on the residue obtained in the above step, using about 50 g of sodium hydroxide.

The final residue of insoluble material amounted to 37 g. In the samples to date, the solution of this final residue in perchloric acid solution and precipitation, using 12 g of oxalic acid, yielded an amount of thorium oxalate equivalent to 8.6 g of thorium metal.

The amount of hydrochloric acid required after the first hydroxide treatment is about 500 ml, and 200 ml is required after the second cycle. Excess hydroxide must be neutralized, and the solution must be made from 1N to 3N in hydrochloric acid before precipitation of the thorium oxalate.

4. QUANTITIES OF MATERIAL REQUIRED AND PRODUCT OBTAINED (PER 1000 GRAMS OF SLAG)

The total amount of thorium recovered was 55 g (as metal), 83.5 per cent of which came from step 2; the remaining 16.5 per cent came from the NaOH treatment. This amount will depend on the efficiency of the reduction process.

The amount of hydrochloric acid required for step 2 was 3300 ml (7.32 lb); for step 3, 700 ml (1.56 lb) was required, giving a total of 4000 ml (8.9 lb).

The oxalic acid required was as follows: step 2, 70 g; step 3, 12 g; total, 82 g.

The amount of sodium hydroxide required in step 3 was 250 g.

Thorium oxalate has been chosen as the final precipitate of the thorium because it can be conveniently converted to thorium fluoride, because it is easily filtered, and because its precipitation offers a convenient separation from iron. The extent of coprecipitation of calcium is small. In an experiment in which 1 per cent of calcium was added to the solution from which thorium oxalate was to be precipitated, there was 100 ppm of calcium in the thorium oxalate.

Oxalic acid is used as the precipitating agent rather than ammonium oxalate since it has been found to give a precipitate which is more easily filtered.

Paper 8.3

PREPARATION OF ANHYDROUS THORIUM FLUORIDE FOR METAL PRODUCTION

By A. S. Newton, Henry Lipkind, W. H. Keller, and J. E. Iliff

[Editor's Note: Work done at Iowa State College. Based on Report CC-2713. Prepared for publication Apr. 25, 1945.]

ABSTRACT

Thorium fluoride suitable for reduction to metallic thorium can be produced on any scale by hydrofluorinating low-burned thoria at 550°C in an apparatus of material which will not reduce hydrogen fluoride, such as graphite, nickel, monel, or magnesium. The fluoride is completely free from oxide. The best results have been obtained by using thoria made by calcining thorium oxalate at 650°C.

The reaction of fluorine on thorium carbide and the reaction of hydrogen fluoride on thorium hydroxide, thorium oxycarbonate, and thorium oxalate have been studied. A wet method of preparation has also been studied.

1. INTRODUCTION

In the preparation of thorium metal by a bomb reduction procedure,¹ it is necessary to have thorium fluoride free from water, thorium oxide, and oxides of other elements. Commercial sources of thorium fluoride gave poor results at best in the reduction, so it was necessary to investigate the preparation of a better grade of thorium fluoride than was obtainable commercially at the time. The problem was assigned to this group, and it was suggested that dry HF be tried on thorium salts (similar to the uranium fluoride process).

Concurrently with the investigation of the methods of preparation, the methods of reduction have been improved, and a satisfactory method of analysis for thorium and fluorine has been worked out. Therefore,

some of the early results obtained might be better than they appeared at the time since the methods then available (reduction methods and analysis) for classifying the material as satisfactory or not were themselves quite unsatisfactory. At present a very satisfactory method for analysis of thorium fluoride is being used.² It involves the hydrolysis of the fluoride with superheated steam at 900°C, condensation and collection of the HF, and titration with a base. The thorium is then determined on the oxide left. The main criteria used in classifying a method of preparation as suitable were purity of product (particularly oxide content), yield on reduction, and bulk density of the product.

2. EXPERIMENTAL WORK

2.1 Reaction of Thorium Carbide and Fluorine. Thorium carbide can be prepared by the reaction of carbon and thorium oxide at high temperatures. The carbide was reacted with fluorine at temperatures up to 550°C in a nickel apparatus. The finely pulverized charges of carbide were spread out in a layer $\frac{1}{4}$ in. deep in a nickel boat, and the whole apparatus was placed in a nickel reaction tube. The fluorine was introduced at 350°C and the temperature raised to 550°C and maintained at that temperature for 6 hr. The reaction

was not complete, and there was some free carbon or thorium carbide mixed with the white fluoride. Conversions of 80 and 89 per cent, respectively, were obtained in two experiments using 100-g charges. The product gave pellets of thorium metal on reduction, using calcium and an iodine booster, but was not considered satisfactory.

2.2 Reaction of Commercial Thoria with Anhydrous Hydrogen Fluoride. Commercial thoria was found to be too high-burned to react readily with hydrogen fluoride at temperatures up to 700°C. Heating at 700°C for 3 hr gave only 90 per cent conversion of a 10-g sample of thoria. The product was sintered and discolored.

2.3 Precipitation of Thorium Fluoride. Thorium fluoride was precipitated from a thorium nitrate solution with hydrofluoric acid using paraffin-lined beakers. The product was filtered and then dried at 100°C for several days; this was followed by drying at 500°C and at reduced pressure for several hours. The analysis gave Th, 76.11 per cent; F, 23.94 per cent. Theoretical values for ThF are Th, 75.33 per cent; F, 24.67 per cent.

Probably some hydrolysis has taken place since the thorium analysis is high and the fluorine analysis low. The method is difficult, how-

ever, and the product is bulky; hence it was not deemed suitable for production.

2.4 Reaction of Commercial Thorium Hydroxide and Anhydrous Hydrogen Fluoride. Mantle-grade thorium hydroxide obtained from the Lindsay Light & Chemical Co. was used. It was quite impure, containing carbonate, calcium, lead, iron, and about 3 per cent sodium. It had a thorium content corresponding to 92 per cent $\text{Th}(\text{OH})_4$.

Small-scale experiments showed that at temperatures around 600°C a product resulted which gave fair reduction to metal. Therefore a larger apparatus was constructed having graphite trays enclosed in a monel bomb; the trays each held about 300 g of thorium hydroxide. The apparatus is shown in Fig. 1. It consisted of a set of 11 graphite trays $1\frac{1}{2}$ in. high, with a bottom $\frac{1}{2}$ in. thick. The bottom had a notch $\frac{1}{2}$ in. wide and $\frac{1}{4}$ in. deep around it to fit into the tray below. The trays are $5\frac{1}{2}$ in. O.D., 5 in. I.D., and the inside depth of the trays was 1 in. Near the side of each tray was a connecting pipe $\frac{3}{4}$ in. high with a $\frac{1}{2}$ -in. hole through which the gas passed from tray to tray. The connecting pipes were placed on alternate sides of the apparatus so that the gas had to pass over the material in each tray. The whole set of trays was placed on two graphite blocks inside a monel-metal shell. The monel shell was 18 in. high, 6 in. O.D., and $5\frac{3}{4}$ in. I.D. A flange 1 in. wide on the bottom allowed a $\frac{1}{8}$ -in.-thick bottom to be held in place. A graphite pipe screwed into the bottom tray, and a nickel lock nut gave a tight connection with the monel shell. A brass fitting that was screwed onto the graphite pipe permitted connection of the HF tank to the trays via copper tubing. The top tray was fitted with a tight-fitting graphite cover onto which a close-fitting graphite outlet pipe was placed. The HF was allowed to escape from this pipe into the atmosphere. The whole apparatus was heated by a resistance furnace. Measurements with thermocouples both inside and outside the monel shell showed a temperature difference of less than 5°C after the furnace had been at 600°C about $\frac{1}{2}$ hr.

In this apparatus, up to 3300 g of thorium hydroxide can be converted at one time; the hydroxide was packed $\frac{3}{4}$ in. deep in each tray. The temperature of introduction of HF, the maximum temperature reached, the temperature at which the apparatus was flushed with nitrogen, and the time required for conversion were all studied. The results can be summarized by saying that temperatures from 300 to 700°C give excellent conversions to the fluoride. The best product from the standpoint of physical properties and appearance was obtained by heating the apparatus to 250°C , introducing the HF, raising the temperature to 550 to 600°C , and keeping it there for 4 hr with an HF flow of about 1 to $1\frac{1}{2}$ lb/hr over the material. The apparatus was flushed with nitro-

gen while at 550°C and allowed to cool with no gas flowing through the apparatus. The fluoride was discolored owing to impurities, and there were black specks of free carbon to be found on top of the material in the trays. The conversion was uniform in all trays if sufficient HF (about 30 per cent excess) was used. A typical analysis for thorium and fluorine of the material prepared from mantle-grade hydroxide is as follows: Th, 69.30 per cent; F, 22.80 per cent.

This accounts for only 92.10 per cent of the material, but the F/Th ratio is calculated to be 4.02. Since the material contains 3 per cent sodium, calcium, lead, and iron as well, the other 8 per cent is probably distributed among these materials. The fluorine in calcium and sodium fluorides is not measured by the hydrolytic method as ordinarily run, so these do not interfere with the F/Th ratio above, even though they are probably converted to fluorides.

This thorium fluoride gave yields, on metal reduction, of 87 to 93 per cent, showing that even considerable impurities of salts do not interfere provided oxides and water are absent. Halides of alkali and alkaline-earth metals are removed in the slag.

2.5 Reaction of Anhydrous Hydrogen Fluoride with Thorium Oxalate, Oxycarbonate, and Oxide. Reactions have been run with thorium oxalate, thorium oxycarbonate, and thorium oxide prepared by the calcination of the above salts. Calcination of either of the salts to the oxide by heating in air to 650°C increases the bulk density considerably, thus allowing a greater charge to be placed in the hydrofluorination apparatus and yielding a fluoride of higher bulk density. The calcined oxalate gave the most dense oxide, and up to 2500 g can be placed in the graphite-tray setup described in Sec. 2.4. The hydrofluorination was carried out as in Sec. 2.4. Typical analyses of the product produced with the above raw material are given in Table 1.

3. SYSTEM USED AT TIME OF WRITING TO PRODUCE ThF_4

Since both nickel and magnesium will effectively resist hydrogen fluoride-water mixtures up to 600°C, these metals may be effectively used as materials of construction. If the fluoride is in direct contact with nickel, it will contain nickel as an impurity in the salt. However, magnesium can be in contact with the salt since any magnesium introduced into the thorium fluoride will be removed in the reduction and casting. The apparatus described below is modeled after that used for producing uranium fluoride at The Harshaw Chemical Co. The hydrofluorination apparatus is shown in Fig. 2. It consists of an electric furnace wound around a 7-in. I.D. iron core (11 ohms, No. 10 chromel A wire, 220 volts). The temperature is controlled by a Capacitrol in

series with the furnace. The reaction chamber is a 6-in. O.D. monel or nickel pipe containing three magnesium trays on which the charge is placed. These trays are formed from $\frac{1}{8}$ -in.-thick AM2S pure magnesium sheet. Since magnesium becomes very soft when annealed, lighter material is not satisfactory. One end of the monel pipe is welded shut with a gas-entrance tube fitted into the center. The other end is closed by a recessed iron plate; the end of the monel tube fits into the recess in the iron plate and is sealed with a paste of calcium fluoride. The iron plate is held in place with two wedges between the plate and a crossbar attached to the monel pipe. A gas-outlet tube is provided in the iron plate. At least 6 in. of free space is provided at each end of the trays to allow proper gas distribution in the chamber.

The HF is provided from a cylinder heated with a water spray at about 27°C (4 lb/sq in. gauge pressure). The HF is metered by a $\frac{1}{16}$ -in. orifice in a platinum disk, which, at this pressure, gives a flow rate of about 3 lb/hr. The excess HF and water are condensed in a washing column and washed down the drain. The whole apparatus is semienclosed in a hood, although, except for the washing tower, there is no HF escape when proper assembly has been made. A nitrogen tank is connected into the system for flushing the reaction chambers before removal from the furnaces.

If desired, two or more of these units can be set up in series, and by properly adjusting the time cycles of operation practically all the HF can be utilized. With a single chamber, about 20 per cent excess HF must be used to obtain complete conversion.

The magnesium trays are packed with thorium oxide from $\frac{3}{4}$ to 1 in. deep, care being taken to leave gas space above the material. In three trays 5 ft long, about 25 lb of thoria constitutes a charge. There is little change in volume of the solid in the conversion from oxide to fluoride. The magnesium sheets as received are coated with a thin yellow film, the result of a chromate treatment by the manufacturer. This causes some surface discoloration of the first few batches run on new trays, but after a few times the product is pure white. The nature of the original discoloration has not been found. It can be removed by heating the fluoride in dry air.

The procedure is as follows: the raw material is thorium oxalate having a composition approximating $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$. This is calcined in nickel trays (bed of solid is 3 in. deep) in an electric furnace. At 500°C a stream of dry air is blown through the furnace to burn all CO and prevent its accumulation. The temperature is raised to 650°C, maintained there for 3 hr, and the material can then be removed from the furnace. Table 2 gives some data on the calcination of thorium oxalate.

The thorium oxide is packed into the magnesium trays as described, and the apparatus is assembled. The reaction chamber is then placed in the furnace, which has been preheated to 550°C, and the HF inlet and discharge connections are made. The temperature, measured between the furnace wall and the reaction chamber, drops about 120°C but returns to 550°C within 1 hr. HF is passed through the apparatus until a 20 per cent excess has been used. The reaction chamber is then flushed with nitrogen, withdrawn from the furnace, and allowed to cool. In about 2 hr the fluoride can be removed and the chambers can be reloaded. The conversion has been shown to be uniform throughout the system. Data for several batches are given in Table 3 and show the analysis of the product from various parts of the system.

From Table 4, it can be seen that the weight change on hydrofluorination is a good index of the completeness of the process. When the weights do not check within a few ounces with a 25-lb charge, the run is repeated.

The yield of metal on reduction of fluoride produced in this manner was consistently 95 to 98 per cent. This shows that the material is well-suited for the purpose.

The impurities which might be introduced in the process are Mg and Ni. It was suspected that the discoloration in the early runs was due to carbon; hence carbon analyses were also run on the fluoride. The results are as follows: The ThO_2 contained 10 ppm of Mg and 100 ppm of C. The ThF_4 contained 14 ppm of Mg and 100 ppm of C. It is apparent that no significant amount of impurities has been picked up from the apparatus.

Table 1—Analyses of ThF_4 from Various Raw Materials

Raw material	Th, %	F, %	Bulk density of ThF_4
Oxalate, atomic-weight grade	75.27	24.52	0.90
Oxalate, atomic-weight grade	75.28	24.63	
Oxalate, atomic-weight grade, calcined	75.25	24.75	1.90
Oxalate, mantle grade			0.67
Oxycarbonate, atomic-weight grade	75.50	24.47	
Oxycarbonate, atomic-weight grade, calcined	75.50	24.52	1.03
Hydroxide, mantle grade	69.3	22.8	2.28
Oxalate, precipitated from thorium nitrate solution			0.93
Oxalate, precipitated from thorium nitrate solution and calcined			1.50
Theoretical for ThF_4	75.33	24.67	

Table 2—Calcination of Thorium Oxalate

Weight of thorium oxalate, lb	Weight of ThO ₂ , lb	Theoretical weight of ThO ₂ from Th(C ₂ O ₄)·2H ₂ O, lb
25.0	14.9	14.87
24.16	14.3	14.35
26.5	15.7	15.77

Table 3—Analysis of ThF₄ Produced in Long Chambers

Single chamber						
Area taken	Batch 1		Batch 2		Batch 3	
	Th, %	F, %	Th, %	F, %	Th, %	F, %
Bottom tray, head	75.30	24.91	75.60	24.32	75.38	24.59
Bottom tray, center	75.48	24.97	75.45	24.88	75.20	24.64
Bottom tray, end	75.30	25.10	75.40	24.66	75.38	24.68
Center tray, head	75.30	25.10	75.30	24.97	75.38	24.64
Center tray, center	75.30	24.83	75.48	25.10	75.30	24.83
Center tray, end	75.48	24.97	75.28	24.55	75.40	24.78
Top tray, head	75.30	24.80	75.37	24.97	75.40	24.66
Top tray, center	75.30	25.10	75.02	24.61	75.38	24.64
Top tray, end	75.60	24.01	75.38	24.65	75.29	24.80

Two bombs in series

Run	Bomb 1		Bomb 2	
	Th, %	F, %	Th, %	F, %
1	75.38	24.63	75.38	24.62
2	75.46	24.72	75.36	24.62
3	75.36	25.20	75.52	24.42
4	75.60	24.58	75.45	24.77

Table 4—Material Balance on Hydrofluorination of ThO₂

ThO ₂ taken, lb	ThF ₄ found, lb	Theoretical ThF ₄ from oxide, lb
27.25	31.70	31.77
26.56	30.80	30.96
20.75	24.20	24.19
18.69	21.75	21.79
20.50	23.87	23.90
19.90	22.58	22.81
18.90	22.30	22.49

Fig. 1 —Apparatus for the conversion of thorium hydroxide to thorium fluoride.

Fig. 2—Hydrofluorination apparatus for the conversion of thorium oxide to thorium fluoride.

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Paper 8.4

PRODUCTION OF THORIUM METAL BY METALLOTHERMIC REDUCTION OF THORIUM FLUORIDE

By F. H. Spedding, H. A. Wilhelm, W. H. Keller, J. E. Iliff,
and Charles Neher

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ABSTRACT

Thorium had previously been prepared in small quantities by the reduction of its halides and oxides by alkali and alkaline-earth metals, by the reduction of its oxide by Ca, and electrolytically. A process is here described by which large quantities of thorium have been produced by the reduction of the tetrafluoride by calcium. It was found necessary to add heat to that of the reaction by carrying out simultaneously an auxiliary reaction in the reaction chamber. The reaction of iodine, bromine, and various halides of volatile metals with Ca produced sufficient additional heat to fuse the slag and the metal. ZnCl_2 proved to be the most effective "booster." Conditions of reduction are described for various scales of operation. The properties of the resultant alloy and the purity of the final product are described.

INTRODUCTION

The need for thorium metal for the investigation of its use as a pile material was understood early in the development of the project. The greater assurance of success and the greater possible speed of achievement of the desired results by the use of uranium placed emphasis on the production of uranium to the exclusion of thorium. However, in-

terest in thorium piles continued and methods for the production of the metal were investigated as time was available. Up to 1942 only small amounts had been prepared, chiefly by the reduction of the oxide with calcium by the method of J. W. Marden of Westinghouse.

1. LITERATURE

1.1 Reduction of Halides. Metallic thorium was first prepared by the potassium reduction of ThCl_4 by Berzelius.¹ A number of other investigators²⁻¹⁰ subsequently produced the metal in various states by the reduction of simple or double halides with alkali or alkaline-earth metals, particularly Na. Von Bolton⁵ succeeded in hammering and rolling metal so produced into spongy wire. Lely and Hamberger⁸ sintered powdered metal into wire by alternating current.

1.2 Reduction of Oxide. The reduction of thoria with carbon was attempted by Moissan and Etard¹¹ and later by Troost.¹² Carbide resulted in all cases. Similarly the reduction of thoria by silicon produced a silicide.¹³ Decompositions of hydrides,⁷ nitrides,¹⁴ sulfides,¹⁵ and other compounds were not fruitful.

1.3 Electrolytic Methods. Thorium of 95 per cent purity was claimed by Moissan and Hoenigschmid¹⁶ by the electrolysis of K_2ThCl_6 at 600°C by 3.5 amp current density at 110 volts with graphite electrodes. Electrolytic thorium was subsequently produced by others.¹⁷⁻¹⁹

1.4 Thermite Process. The reduction of thoria by alkali metals failed, but alkaline-earth metals, particularly Ca, gave powdered metal.^{20,21} The thermite reaction with aluminum or magnesium^{4,22,23} gave beads of thorium in the sintered mass, and Kuhne²⁵ claimed to have produced reguline thorium by adding some chlorate to the thermite mixture of Goldschmidt.

The production of thorium up to 1924 is fully summarized in Gmelins Handbuch.²⁴

1.5 Reduction of Oxide with Ca by Marden. At the beginning of the project the most fruitful procedure for the production of thorium was the reduction of ThO_2 by Ca as developed by Marden.²⁶ ThO_2 is mixed with Ca metal and CaCl_2 and heated to red heat in a sealed bomb. Thorium and calcium oxychloride result. The product is leached with water and the thorium is obtained in powdered or granular form. The powdered metal is pressed into rods and sintered into a coherent form at about 1300°C. This product can be extruded, rolled, or otherwise worked.

2. APPLICATION OF METALLOTHERMIC PROCESS AT IOWA STATE COLLEGE

The production of massive thorium metal by the process used at Iowa State College for the production of uranium²⁷ with calcium was

attempted.²⁸ ThF₄ was mixed with 20 to 40 per cent excess Ca and heated in a refractory-lined steel bomb until reaction occurred. Only powdered metal was obtained. The heat produced by the reaction added to that supplied by preheating the reactants was not sufficient to fuse the metal produced. The melting point of thorium about (1800°C) is much higher than that of uranium (1120°C), and the reduction of its tetrafluoride produced less heat than does the reduction of UF₄. It appeared that more heat would be needed to melt the products of the reaction. The use of auxiliary oxidants or "boosters" in the production of uranium by the magnesium method²⁹ and of such boosters in the small-scale production of uranium by the use of Ca (reference 30) suggested its use with Th.

2.1 Heat Available and Required. The heats of reaction at 298°K of the reductions of some thorium halides by Ca and Mg are as follows:

A consideration of the heats of reaction involved showed that the reduction of ThF₄ by Ca will not produce sufficient heat to melt the products. Mg will not spontaneously reduce ThF₄. Therefore the reduction by Ca could best be accomplished with the aid of a booster or of sufficient preheat or both. It was found experimentally that sufficient heat to melt the products could not be added by preheating a mixture of the reactants before reaction occurs. Hence experiments were started with boosters.

The incomplete fusion of the slag in the reduction of ThF₄ by Ca indicated that the heat of reaction, 30 Kcal per mole of ThF₄, had raised the temperature of the charge only a few hundred degrees, possibly from about 500 to about 1200°C, or 700 degrees. If it were necessary to raise the temperature to 1800°C, an increase of 1300 degrees would be required, or nearly two times the heat supplied by the heat of reaction (the heat of reaction supplied by preheating would remain constant). Since the products of the auxiliary or booster reaction would absorb some heat, even more additional heat would be required.

2.2 Use of Boosters. Iodine had been found to be an excellent booster in the small-scale production of uranium.³⁰ The reduction of

I_2 by Ca produces 129 Kcal per mole of I_2 . Since more than twice the heat of reaction of ThF_4 plus Ca (30 Kcal) seemed to be needed, $\frac{1}{2}$ mole of I_2 (65 Kcal) per mole of ThF_4 was tried first as a starting point for determining the amount of booster required.³¹ On the 50-g scale (to produce 50 g of metal as theoretical yield) only spongy metal was produced. On this scale the heat loss is proportionately very great compared with large-scale production.

(a) $KClO_3$ and $Th(SO_4)_2$ as Boosters. It was decided to obtain enough heat to fuse the products by a combination of I_2 and $KClO_3$ as boosters.³¹

As a trial quantity 1 mole of I_2 and $\frac{1}{3}$ mole $KClO_3$ were used per mole of ThF_4 , supplying $128.6 + 156.5 = 285.1$ Kcal per mole of ThF_4 . This experiment was conducted in a $1\frac{1}{2}$ -in. bomb, on which scale of operation the relative heat loss is very great, and with ThF_4 containing 12 per cent of unconverted oxide. In spite of the addition of several times the assumedly needed quantity of heat, the metal was not well fused. However, small pellets (up to 3 mm diameter) of a clean fused metal were produced. It was demonstrated that the metal could be produced and fused by the bomb process. Increasing the scale and improving the reactants would lower the booster requirement and result in massive metal.

Since $Th(SO_4)_2$ supplies much more heat per mole of Th than does ThF_4 on reduction by Ca (700 to 30 Kcal),³¹ it was thought that it might serve both as a booster and as a source of Th.

One-half mole of $Th(SO_4)_2$ per mole of ThF_4 was reduced by Ca on the 50-g scale. No massive metal was obtained. The reaction was repeated with 1 mole of I_2 in addition to $\frac{1}{2}$ mole of $Th(SO_4)_2$ per mole of ThF_4 , but again no massive metal was obtained. Far more heat was produced than should have been necessary to melt the products; therefore it appeared that the stiffening of the slag by the large amount of CaO produced by the reduction of the sulfate prevented the agglomeration of the metal.

(b) Successful Reduction with Iodine. More heat appeared to be needed and yet $KClO_3$ and $Th(SO_4)_2$ both seemed to produce more oxide than could be tolerated. Iodine, however, lowered the melting point of the slag by the fluxing action of the iodide. Since $\frac{1}{2}$ I_2 per mole of

ThF_4 had been found to be very inadequate, it was empirically decided to try 3 moles of I_2 per mole of ThF_4 .³¹ Although this ratio produced far more heat than appeared necessary, the heat loss was so great on a relatively small scale that a large excess was required. A yield of 80 per cent of pellets of ductile metal which analyzed 95 per cent Th was obtained with 3 I_2 per mole of ThF_4 on a 25-g scale, using commercial ThF_4 supplied by the Lindsay Light & Chemical Co. and dried in vacuo at 500°C. The experiment was repeated with only 2 I_2 per mole of ThF_4 with no agglomeration of metal.

Since the type of liner, liner thickness, preheating procedure, and other variables needed fixing for the production of optimum yield, a ratio of 3 moles of I_2 per mole of ThF_4 , with 20 per cent excess Ca in the 3-in. bomb holding a charge of 7.5 g of ThF_4 , was arbitrarily adopted for further experimentation.

2.3 Early Preparation of ThF_4 . Erratic results in the preliminary experiments indicated that the fault lay in the low purity of the thorium tetrafluoride. The salts were not dry and contained 3 per cent or more of oxide; hence it was decided to prepare salt for the reductions. Various procedures were attempted, but the best results were obtained by the passage³² of HF over $\text{Th}(\text{OH})_4$. The hydrofluorination was conducted in a series of round graphite trays, each tightly fitted into the tray above and that below and drilled on alternate sides with $\frac{1}{2}$ -in. holes to permit the flow of gas from tray to tray across the surface of the charge. These trays were enclosed in a graphite cylinder with well-fitted heads, through which the gas was introduced and discharged by graphite tubes. The gas was introduced at the bottom of the chamber and passed successively over the surface of the charge of $\text{Th}(\text{OH})_4$ in each tray, and the excess was discharged at the top along with the water formed in the process. The entire assembly was heated in a vertical resistance furnace. HF was introduced at 350°C, and reaction began at once, as shown by the evolution of water and the complete absorption of the HF introduced. The temperature was increased from 350 to 680°C in $4\frac{1}{2}$ hr, at which time no water was given off, indicating completion of the reaction. ThF_4 prepared in this fashion produced yields of 78 to 80 per cent of massive thorium, whereas the commercial fluoride produced yields of only 40 to 55 per cent.

Following preliminary preparations by some of the authors, the preparation of ThF_4 by the above process was standardized and expanded by Newton and Lipkind³³ and has been used in producing the fluoride at Iowa State College in large quantities. The specifications of ThF_4 finally adopted for production and the effects of various properties and of composition will be treated in detail later in this

paper. However, early experiments on a small scale using 3 moles I_2 per mole of ThF_4 with 40 per cent excess of Ca in sintered-lime bomb liners produced the following yields with different lots of ThF_4 prepared by various processes from different source materials:³²

Source of ThF_4	Treatment (at 500°C)	Yield, %
Lindsay Light & Chemical Co., West Chicago, Ill.	Dried in vacuo	56–63
Maywood Chemical Works, Maywood, N. J.	Dried in vacuo	41–55
Iowa State College, Ames, Iowa	Prepared by $HF + Th(OH)_4$	64–80

After standardizing to some extent the fluoride being used, the effect of the type of refractory liner used in the reaction chamber was next investigated. Bomb liners were applied either by jolting lime in the bomb or by inserting sintered-lime crucibles.

In general the use of sintered liners with fixed conditions and materials gave a 10 to 20 per cent increase in yield over that of the jolted-lime liners.

2.4 Other Halogens as Boosters. (a) Chlorine. Following preliminary production of ThF_4 by various methods, fairly uniform material was produced from Lindsay $Th(OH)_4$, on which reduction studies were made with various boosters. The use of $KClO_3$ was found undesirable because of the high viscosity of the slag resulting from the CaO formed in the reaction of Ca and $KClO_3$. The use of iodine was disadvantageous because of the great volume occupied by the iodine and its equivalent calcium in the quantities required (3 moles of I_2 per mole of ThF_4) and because of the consequent dilution of the ThF_4 . Since chlorine would add much more heat per gram of chlorine used, and some more heat per gram of calcium used, and since the chlorine could be added as a gas at the time of reaction, thus occupying no space in the original charge, it appeared very likely that chlorine would have considerable advantage over iodine.

$$\text{Heat produced per gram of Ca with iodine} = \frac{128.6}{40.08} = 3.17$$

$$\text{Heat produced per gram of Ca with chlorine} = \frac{190.7}{40.08} = 4.75$$

$$\text{Heat produced per gram of iodine} = \frac{128.6}{154} = 0.821$$

$$\text{Heat produced per gram of chlorine} = \frac{190.7}{71} = 2.69$$

Hence 1 mole of calcium used with chlorine is equivalent to $190.7/126.6$, or 1.5 moles of calcium used with iodine, which means that only two-thirds as much calcium is required to produce the same amount of heat.

It was proposed to admit the chlorine as gas into the bomb at the reaction temperature just prior to the expected time of reaction. To accomplish this a steel reservoir was constructed which held the necessary quantity of chlorine at tank pressure and at room temperature. This reservoir was evacuated, filled with chlorine from the tank, and closed off from the tank by a valve. After the bomb and charge had been heated to reaction temperature, a few minutes before ignition was expected, the valve in the line from the reservoir to the bomb was opened, and chlorine was admitted to the reaction mixture. Reaction occurred immediately and yields of 40 per cent were obtained.^{34,35} The metal was spongy and further attempts failed to improve the yield. Because of the complexity of the assembly, the chlorine procedure was suspended for the time.

(b) Bromine. Since bromine is in the liquid state at room temperature, it is considerably more convenient to handle and use than chlorine, but less so than iodine. However, its heat production is greater than that of iodine, although less than that of chlorine.

Since 3 moles of I_2 were required per mole of ThF_4 , $2\frac{1}{2}$ moles of Br_2 per mole of ThF_4 should give about the right amount of heat. Heats of formation of $CaCl_2$, $CaBr_2$, and CaI_2 are -190.7 , -162.2 , and -128.6 Kcal, respectively.

The charge was composed of ThF_4 with 20 per cent excess Ca, as usual, packed in a bomb with jolted liner. The bromine was placed in gelatin capsules or glass vials in various parts of the charge.

Yields produced by the placing of the bromine in various locations are as follows:

Location of bromine	Per cent of yield
1. In gelatin capsule at bottom of charge	0
2. In gelatin capsule at top of charge	25
3. In sealed glass vial at center of charge	21
4. In open glass vial on top of charge	50

The metal produced was in all cases pellets of low yield or mossy lumps, with no case of a single massive ingot. There was evidence of excessive bromine pressure, the bottoms of the bombs in two cases being considerably bulged out. Because of the low yields of poor metal, the inconvenience of handling, and the apparent pressure, further investigation of the bromine reaction was suspended for the time being.

3. HALIDES OF VOLATILE METALS AS BOOSTERS

The halogens were better boosters than oxy-compounds since halides or mixtures of halides were lower-melting than oxides or halide-oxide mixtures. However, relatively low heat produced by iodine in proportion to its weight and bulk was disadvantageous, bromine was not satisfactorily controllable in the reaction, and chlorine offered mechanical difficulties. Moreover, the melting point of thorium is relatively high (about 1800°C).

Since the melting points of alloys of thorium might be expected to be lower and since the halides of some metals have very low heats of formation, the use of the halide of a volatile metal which forms a low-melting alloy with thorium would help to solve both the slag and metal-melting difficulties.³⁴ The desirability of using such a compound would be dependent on the ability to remove the alloying metal by vacuum heating.

An examination of the heats of formation of the chlorides and fluorides of some of the more volatile metals shows that those of Zn, Bi, Pb, and Cd are of interest, provided the metal can be removed by vacuum distillation. The heats of formation and heats of reaction with Ca per equivalent are given in Table 1.

From the point of view of the heats of formation the chlorides listed are desirable in the order Bi, Pb, Cd, and Zn. The fluorides are not as available but could be prepared and would produce more energy. The chlorides would be preferable, however, because of the formation of a mixed halide slag composed of chloride and fluoride, which would have a lower melting point. Availability, purity, and convenience in handling and using also must be considered. Both lead and zinc chlorides were found to be available in adequate purity and quantity. Since cadmium is so very deleterious in some connections, it was felt best to avoid its use, although it can be quantitatively removed by vacuum distillation.

3.1 Bismuth Fluoride. Since bismuth fluoride was available, it was first tried as a booster.³⁴ The salt was ground to 100 to 200 mesh and mixed with ThF₄ and Ca in the desired proportions. These charges of 100 to 200 g of ThF₄ contained 30 per cent excess Ca over that re-

quired for the reduction of the oxidants and were fired in sintered-lime liners in steel bombs. Results obtained with the various ratios of BiF_3 to ThF_4 are tabulated in Table 2. Less than 1 mole of BiF_3 per 3 moles of ThF_4 resulted in poor separation, but 1 to 2 moles of BiF_3 per 3 moles of ThF_4 resulted in fair separation of products. Yields were not encouraging, however.

One mole of BiF_3 per 3 moles of ThF_4 produces an alloy containing 23 per cent by weight of Bi, however, and this presents serious problems in remelting and casting. Any greater amount of Bi would be greatly in the way in casting and very uneconomical in the purchase of materials. Less than this amount appeared useless in achieving separation of the metal and slag.

On remelting in vacuo at 1800°C only about one-half of the Bi was removed, 11 per cent by weight being found in the cast metal. Moreover, the product was brittle, pyrophoric, and reactive with the moisture of the air. For these reasons investigation of the use of BiF_3 as a booster was suspended.

3.2 Lead Chloride. Since the use of a fluoride produced a slag of a single component it appeared desirable to produce a lower-melting slag of two components by using a chloride booster. Lead chloride was available in high purity and was first tried for the purpose. The proportion of lead chloride to be used was investigated by mixing the dry salt with charges of 100 to 200 g of ThF_4 with 30 per cent excess Ca over the theoretical value. These charges were fired in sintered-lime liners in closed steel bombs by heating in a resistance furnace at about 600°C . Results obtained with various proportions of PbCl_2 were as given in Table 3.

Less than 1 mole of PbCl_2 per 2 moles of ThF_4 gave no indication of producing separation of metal and slag. Even 2 moles of PbCl_2 per 3 moles of ThF_4 gave only poor yield. One mole of PbCl_2 per mole of ThF_4 was necessary to give a nearly quantitative yield, and even this metal was not of good quality. Such a ratio represents almost 50 per cent lead, which was neither economical nor desirable. On casting, considerable lead remained in the cast product. Work was discontinued on the use of PbCl_2 as a booster for these reasons.

3.3 Zinc Chloride. Zinc chloride was available in high purity as the partially hydrated salt. This could be dried by heating under an atmosphere of dry HCl . An examination of the heats of formation given in Sec. 3 shows that ZnCl_2 does not produce as much heat per equivalent as do some of the other halides of volatile metals, but it does produce more heat per weight used. Moreover, it has a boiling point of only 900°C at 1 atm against 1500°C for Bi and 1600°C for Pb. Hence it would presumably be much more easily boiled out.

On the basis of the results with PbCl_2 and BiF_3 it was decided to begin the investigation of ZnCl_2 at 1 mole of ZnCl_2 per 2 moles of ThF_4 . On 200- to 400-g charges of ThF_4 with 0.5 mole of ZnCl_2 per mole of ThF_4 and 20 per cent Ca excess heated in sintered-lime liners, yields of 56 to 86 per cent were obtained in preliminary experiments.^{35,36} The alloy was a silver-white brittle mass which corroded rapidly on standing in air, decrepitating to a black powder. Separation from slag was quite sharp, and the ingots of alloy were very easily cleaned by chipping and brushing. They could not be cleaned by leaching in water, however, because the alloy was very reactive with water.

The zinc used as a booster remained almost quantitatively in the thorium alloy in the separation of products in the bomb reaction. Subsequent typical analyses showed the following compositions of the alloy and of the charges from which they were prepared:

Zn in charge, %	Zn in alloy, %
17.1	17.45
12.0	11.55

On remelting in vacuo at 1650 to 1800°C, zinc was found spectrographically to have been almost completely removed (less than 200 ppm, usually less than 100 ppm in cast metal).

4. ESTABLISHMENT OF OPTIMUM CONDITIONS

4.1 Booster Ratio. The determination of the optimum booster ratio was conducted under the conditions prescribed above (200-g charge, 20 per cent excess Ca, sintered liner, furnace at 600 to 650°C).³⁶ The results appear in Table 4. Although the yield from the 0.25-mole ZnCl_2 mixture appeared greatest, separation had been incomplete, and the product contained slag. One-half mole of ZnCl_2 per mole of ThF_4 appeared to be the optimum ratio in which to use ZnCl_2 as booster under the prescribed conditions.

4.2 Excess Calcium. Since the excess reducing metal had been found to be critical in bomb reactions, a series of experiments were conducted using 1 mole of ZnCl_2 per 2 moles of ThF_4 and varying the calcium excess from 0 to 30 per cent with the results shown in Table 5.³⁶ Thus it appeared that at least 20 per cent excess Ca was desirable, and in succeeding experimental work this quantity was used.

4.3 Method of Preparation of Thorium Fluoride. During all this experimental period thorium fluoride prepared in small batches by different procedures from various source materials had been used.

Having established a fairly successful and consistent process for the production of metal from fluoride, it was next decided to evaluate the methods of producing fluoride by the reduction, under fixed conditions, of fluorides prepared by different procedures from all available and usable compounds from various sources. The preparation of the fluorides is fully described elsewhere.³³

Thorium hydroxide, oxycarbonate, and oxalate appeared to be the most suitable of the available compounds. The hydroxide can be hydrofluorinated directly with HF at 500 to 700°C. The oxalate and oxycarbonate can be hydrofluorinated directly, although they are best converted first to the oxide by calcination at 650°C and then hydrofluorinated at 550°C. The hydrofluorination was accomplished either in graphite vessels or in magnesia trays in a monel chamber heated by a chromel-wound furnace.

Various lots of ThF₄ prepared from these source materials were reduced with 20 per cent excess Ca with 0.5 mole of ZnCl₂ per mole of ThF₄ in sintered-lime liners, as shown in Table 6.

It appeared that the carbonate was much better than the hydroxide and slightly better than the oxalate as a base material for the preparation of the fluoride. However, the oxalate is produced in a purification process and is much more readily available. It would be the product finally produced in an extraction-column purification of thorium such as was later used for removal of the rare earths. Hence it was decided to produce all subsequent fluoride from the oxalate, either purchased as such or produced in the purification process.

4.4 Variation of Conditions with Scale. The variation of conditions with scale of operation remained to be studied. In most bomb reductions it had been found possible to decrease both the proportion of booster used and the excess of reducing metal. Having established consistent supplies of raw materials, the variation of booster ratio with scale was next investigated.

On the 100- to 200-g scale, 0.5 mole of ZnCl₂ per mole of ThF₄ was required. On the 300-g scale, 0.33 mole of ZnCl₂ per mole of ThF₄ produced maximum yields. On subsequent reductions in 4- and 6-in.-diameter bombs holding charges of 6 to 30 lb of ThF₄, the booster ratio was further decreased to 0.25 mole of ZnCl₂ per mole of ThF₄. Owing to occasional incompleteness in the hydrofluorination process, from 1 to 7 per cent of oxide may be present in the ThF₄. For this reason 0.3 mole of ZnCl₂ per mole of ThF₄ was adopted as standard, and subsequent large-scale reduction has been done on this basis.

The excess Ca was also decreased on the 6- to 30-lb scale to 15 per cent in some cases, although again the variation of the ThF₄ caused the adoption of 20 per cent for standard procedure.

5. CURRENT METHOD OF PRODUCTION OF THORIUM

Considerable quantities of thorium have been produced using the above procedure in refractory-lined steel bombs $2\frac{1}{2}$ in. in diameter by 12 in. long, 4 in. in diameter by 24 in. long, and 6 in. in diameter by 40 in. long which produce ingots of 1, 6, and 22 lb, respectively, of 93 per cent Th alloy (7 per cent Zn).

The $2\frac{1}{2}$ - and 4-in. bombs are lined with sintered liners of highly calcined high-calcium lime or of electrically fused dolomitic oxide fired in graphite heaters in the induction furnace at 1750 to 1800°C. The refractory is jolted on a pneumatic jolting table into the annular space between a graphite mandrel and the wall of a cylindrical graphite crucible or form, the mandrel is removed, and the liner is fired in the induction furnace, using the graphite form as the heater. These bodies shrink from 7 to 10 per cent on firing, and consequently it is necessary that the mandrel and form be proportionally larger than the desired body. The fabrication and firing of these bodies is described fully elsewhere.³⁷

The charge consists of ThF_4 , Ca, and ZnCl_2 . The ThF_4 is produced by the hydrofluorination at 550°C of thoria made by the calcination at 650°C of oxalate precipitated from column-purified thorium nitrate.^{38,39} The fluoride is ground to 100 to 300 mesh in a Mikro-pulverizer. Distilled electrolytic calcium, 10 to 40 mesh, is used in 20 per cent excess of the theoretical quantity required for the reduction of ThF_4 and ZnCl_2 . The zinc chloride is dried by fusing under HCl for 3 to 4 hr, ground and weighed in the dry room, and mixed with the charge immediately before introducing the latter into the lined bomb. The ZnCl_2 is used in the proportion of 0.29 ZnCl_2 per mole of ThF_4 . A typical charge for a $2\frac{1}{2}$ -in. bomb contains 450 g of ThF_4 , 57.5 g of ZnCl_2 , and 167 g of Ca.

The 4-in. bomb is loaded and fired similarly to the $2\frac{1}{2}$ -in. bomb. A typical charge for the 4-in. bomb contains 8.13 lb of ThF_4 , 1.0 lb of ZnCl_2 , and 2.9 lb of Ca.

The procedure of loading and firing the 6-in. bomb is exactly that which was employed in the production of uranium by the reduction of UF_4 by Mg. This procedure has been described in detail elsewhere²⁹ but may be summarized as follows:

The 6-in. bomb is lined with powdered refractory jolted directly into the bomb. Either highly burned high-calcium lime or electrically fused dolomitic oxide may be used. The refractory is packed by means of a pneumatic jolting table into the annular space between a chromium-plated steel mandrel and the bomb. The mandrel is then removed and the liner used without further burning. The charge is mixed in a MacLellan batch mixer and poured into the bomb through

a funnel reaching almost to the bottom of the bomb, in such a manner as to prevent damage to the liner. The charge is then covered with a disk of sintered refractory or of graphite, which in turn is covered with lime. The bomb is closed by a blind flange bolted to the companion flange fitted to the bomb.

The bomb is placed in a gas-fired furnace at 1050 to 1100°F, and reaction occurs in 30 to 35 min. On cooling, the cover is removed from the bomb, the liner chiseled out by a pneumatic chisel, and the ingot of alloy removed by jolting the inverted bomb on a pneumatic jolter.

A typical charge for a 6-in. bomb contains 30.0 lb of ThF_4 , 3.86 lb of ZnCl_2 , and 10.7 lb of Ca.

The Th-Zn alloy produced in the above process contains about 8 per cent Zn when 0.3 mole of ZnCl_2 per mole of ThF_4 is used. The alloy is silver-white, brittle, and reactive with water and with moisture in the air. It seems to remain unchanged in dry air, as in a desiccator. Because of its reactivity it cannot be cleaned of slag by leaching but must be cleaned mechanically, as by chipping or brushing. Nor can it be exposed to undried air but must be kept in dried air, inert gas, or under oil.

The alloy can be melted in vacuo or under an inert atmosphere such as argon. On heating the alloy in vacuo the zinc boils out, beginning to distill from the solid at about 900°C and distilling rapidly at about 1200°C. The remaining thorium may then be melted and cast into desired shapes. Methods of casting and properties of the cast metal are described elsewhere.⁴⁰

6. PURITY OF THORIUM PRODUCED BY METALLOTHERMIC REDUCTION

The purity of thorium for pile use is of utmost importance. Approximately the same purity is required as is required of uranium plus virtual freedom from uranium in some cases, in order that the other isotopes of uranium being produced will not be diluted with U^{238} .

The first step in the purification was the column extraction of thorium nitrate with hexone as developed at Iowa State College.³⁹ In this process thorium was separated from rare earths, iron, cadmium, and most of the other metals by extraction of commercial thorium nitrate with hexone using calcium nitrate as a salting-out agent. Thorium was precipitated from the purified nitrate solution as the oxalate, by which about 90 per cent of the uranium present was removed. The oxalate was calcined at 650°C to thoria, which was hydrofluorinated at 550°C to form ThF_4 . Boron was removed in the latter step. Any residual cadmium was removed on casting the metal in

vacuo. As a result of these procedures large quantities of metal have been produced with purity within the limits listed in Table 7.

It will be observed that boron is usually less than 0.5 ppm, the greater portion of which is picked up in the casting process. Cadmium is less than 0.2 ppm on metal from column-purified salt and probably less than 0.1 ppm. The method of determination is being further refined. Determination of rare earths is now in process. It will also be seen that the zinc is almost completely removed (less than 5 ppm) when casting conditions are satisfactory.

The reaction of thorium with the oxide refractories, even beryllia, on melting introduces considerable oxide (1 to 3 per cent) into the cast metal. Carbon volatilizes from the graphite heater, introducing sufficient carbon to produce 1 to 3 per cent of carbide. As a result 1 to 6 per cent of combined thorium may be present under operating conditions to date. From 0.06 to 0.2 per cent Be is also picked up from the crucible. The investigation of other refractories and the improvement of vacuum techniques are under way to decrease these reactions.

The composition of the metal with respect to thorium and major impurities is presented in Table 8.

The decrease of the oxygen content of thorium can be achieved by the use of high vacua (now in process of development at Iowa State College) and by better control of temperature. Reaction with the crucible can be decreased considerably by using the minimum temperature (1780 to 1800°C) necessary for free flow of metal. However, the zinc distilled out of the metal interferes with thermocouples to such an extent that measurements are frequently inaccurate and excessively high temperatures are reached. The shielding of the thermocouple is being improved to remedy this defect. The use of self-induction offers some possibility of eliminating carbon. These problems will be discussed in full in the paper on casting.⁴⁰

Table 1*

	Heat of formation of booster per equivalent, Kcal	Heat of reaction per equivalent with $\frac{1}{2}\text{Ca}$, Kcal
BiCl_3	-30	-65.4
PbCl_2	-42.9	-52.5
CdCl_2	-46.5	-48.9
ZnCl_2	-49.8	-45.6
PbF_2	-79.7	-63.3
ZnF_2	-98.0	-55.0

* $\Delta H(\frac{1}{2}\text{CaCl}_2) = -95.4 \text{ Kcal}$; $\Delta H(\frac{1}{2}\text{CaF}_2) = -143 \text{ Kcal}$.

Table 2

Moles of BiF_3 per mole of ThF_4	Yield (Th-Bi alloy), %	Quality
0.25	37	Poor separation, slag inclusions
0.33	55	Clean, massive metal
0.33	67	Clean, massive metal
0.67	65	Clean, massive metal

Table 3

Moles of PbCl_2 per mole of ThF_4	Yield, %	Condition of metal
0.20	0	No separation from slag
0.33	0	No separation from slag
0.50	25	Pellets
0.67	25	Pellets
1.00	~100	Poor, with inclusions of slag

Table 4

Moles of ZnCl_2 per mole of ThF_4	Yield, %	Condition
0.25	75	Slag inclusions
0.50	64	Clean metal
0.75	62	Clean metal
1.00	27	Brittle, reactive

Table 5

Excess Ca, %	Yield, %
0	45
10	47
20	83
30	83

Table 6

Thorium tetrafluoride lot No.	Source	Yield of alloy, %
Hydroxide		
5	Th(OH) ₄	73
6	Th(OH) ₄	72
7	Th(OH) ₄ fused	77
9	Th(OH) ₄ blend	81
13	Th(OH) ₄ blend	84
17c	Th(OH) ₄ predried	56
18c	Th(OH) ₄ predried	69
Oxalate		
14a	Th(C ₂ O ₄) ₂	92
Carbonate		
14	Th(OCO ₃) (approx.)	95
17a	Th(OCO ₃) (approx.)	91
17b	Th(OCO ₃) predried	94
18a	Th(OCO ₃) predried	88.5
18b	Th(OCO ₃) predried	91.5

Table 7—Purity of Cast Thorium Metal Made from Column-purified Salt

Impurity	Lower limit, ppm	Upper limit, ppm	Usual content, ppm
C	500	2000	1200
N	200	800	350
Al	100	700	300
Si	100	700	300
Zn	<5	100	<5
Fe	40	125	
Ca		<25	
Mg		<30	
Ba		<25	
Na	5	15	
Mn	1	7	3
Pb		<5	
K	5	10	
Li		<2	
B	0.3	1.5	<0.5
Cd		<0.2	<0.2
U		0.2	<0.2

Table 8—Major Components of Cast Thorium Metal

Component	Lower limit, %	Upper limit, %	Usual content, %
Thorium (free)	94	99	97.8
Thorium (combined)	1	6	2
Thorium (total)	95	99	99
Beryllium	0.02	0.08	0.06
Nitrogen	0.02	0.08	0.035
Carbon	0.05	0.2	0.12

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Paper 8.5

CASTING OF THORIUM METAL AND SOME
PROPERTIES OF THE CAST METAL

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[Editor's Note: Work done at Iowa State College. Based on Reports CT-1780, CT-1784, CT-1977, CT-2943, and CT-2951. Prepared for publication Oct. 2, 1945.]

ABSTRACT

Methods of casting thorium metal produced by the metallothermic reduction of ThF_4 by Ca with various auxiliary oxidants are described. Graphite was found to be reactive with thorium at the flowing temperature of the metal produced. Refractory oxides of the alkaline-earth metals were found usable as ceramics; BeO was best. Casting was done at 1800°C . The accurate measurement of temperature in this region is difficult, and a W-Nb thermocouple was developed for the purpose. The Zn from the ZnCl_2 used as a booster shorted out the couples, requiring specially fabricated BeO shielding for their protection.

The metal was cast in vacuo by melting in a BeO crucible at 1800°C and by permitting it to flow freely, without the use of a valve, through a hole in the bottom of the crucible into a BeO mold, also maintained at 1800°C . Metal was also cast by melting in situ in BeO crucibles without flow or pour; the melting crucible also served as a mold. The Th-Zn alloy (7 per cent Zn) produced by the booster reaction was also melted at 1200°C in argon without perceptible loss of zinc for the production of desired shapes of the alloy to be used in further casting.

The melts were made by induction heating using graphite heaters. BeO, MgO, and other oxide refractories were used for insulation.

Carbon black was avoided because of the resultant carburization of the metal by the flying carbon dust. Insulation was done both by the use of shields and by loose-packed oxides. Cylinders, hemispheres, and rectangular shapes weighing from 1 to 70 lb were cast by these procedures.

The cast metal when analyzed gave 99 to 99.5 per cent thorium, usually 97 per cent free metal. The purity of the metal is described. Some physical properties are presented, and the working and shaping of the metal are discussed here.

Thorium was produced at Iowa State College by the reduction of ThF_4 by Ca using ZnCl_2 as an auxiliary source of heat, or booster.¹ An alloy of Th and Zn was produced by this reaction which contained from 6 to 15 per cent Zn according to the amount of booster used. The greater portion of the metal produced contained 7 per cent zinc. Before this metal could be used for physical or chemical investigations or for fabrication purposes it was necessary that the zinc be removed and that it be cast into the desired shapes. Removing the Zn by melting in vacuo and casting the purified melt proved the simplest means of achieving these objectives.

1. REFRACTORIES USED IN CASTING THORIUM

The discovery of materials sufficiently refractory and inert for use in forming melting crucibles and molds was the first problem in the casting of thorium.

1.1 Graphite. Since graphite is quite refractory, available in sufficient purity, and readily shaped by sawing, machining, drilling, etc., its use would have been very desirable. Carburization usually occurred, however, on melting the metal in graphite. Carburization does not occur perceptibly until the metal is somewhat above its melting point, but the difficulty of exact temperature measurement and control in the range of 1800°C causes the necessity for very close control to be undesirable. Above 1800°C the reaction with graphite progresses readily to form the carbide.²⁻⁴ The gain in carbon content on heating the metal in graphite is approximately 0.2 per cent up to 1600°C, 0.6 per cent at about 1650°C, and complete carburization at 1800°C or above if heated for a sufficient time. The carbide is very hard and brittle and slakes on standing in air. Further investigation of the use of graphite was suspended after the observation of the above reactions.

1.2 Refractory Oxides. Crucibles and molds of certain of the refractory oxides were next investigated. The method of fabricating these bodies is described elsewhere.⁸ Since lime and magnesia had been used in the melting of uranium and other metals,⁵⁻⁷ they were

first tested. Thorium reacted in vacuo with magnesia at about 1650°C and with lime at about 1750°C.²⁻⁴ This was to have been expected owing to the great volatility of Mg and of Ca. Since it was found that temperature of about 1800°C was necessary for achieving the free flow of thorium, magnesia and lime were shown to be unusable.

Thoria^{2,4} was tried as a melting crucible with little attack at the melting point, but considerable attack was noted at the somewhat higher temperature necessary for efficient casting. The solubility of thorium in thorium would indicate this result. Zirconia showed little attack but was much more difficult to fabricate by the jolt-pack method than other oxides and hence was not employed in the early work with thorium.

1.3 Beryllia. Although much less available than magnesia or lime, beryllia was found to be much less reactive in vacuo at high temperature because of the lower volatility of beryllium. Moreover, it can be fabricated into stronger ware which offers great resistance to thermal shock and is unaffected by moisture, and the ware retains its shape and shrinks more evenly on firing.⁸ On heating thorium in beryllia, the in vacuo reaction was found to be negligible up to 1775°C and only slight at 1800°C.²⁻⁴ However, it increases fairly rapidly above 1800°C, and by 1900°C erosion of the melting crucibles has been found to have progressed as much as $\frac{1}{16}$ in.

2. CASTING TEMPERATURE IN VACUO

2.1 Melting Point of Thorium. The melting point of thorium has been variously reported from as low as 1450°C (reference 9) to as high as 1845°C (reference 10). Values of 1672 to 1739°C are reported by Thompson.¹¹ These discrepancies are partly due to the fact that accurate thermometry in the range of 1600 to 2000°C is much more difficult than in lower ranges. Moreover the determination of the melting point of thorium offers special difficulties resulting from the physical and chemical properties of the metal. Further investigation is under way on the accurate determination of the melting point.

In spite of the uncertainties in the melting point of thorium, however, the temperature at which the metal flows readily can be empirically determined quite simply. By melting large masses (10 to 50 lb) in crucibles with 1- to 1½-in. holes in the bottom, it has been found that the metal does not flow, even though the surface was well cleaned and in good vacuum, until a temperature of 1775°C is reached. Hence 1800°C has been adopted as the casting temperature for this work.

2.2 Thermocouples. The measurement of temperature in the range above 1600°C offers much greater difficulty than in the range

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2.2 Thermocouples. The measurement of temperature in the range above 1600°C offers much greater difficulty than in the range

of the melting point of the more common metals. The usual thermocouples do not function above 1600°C , and optical pyrometry requires clear and unobstructed vision, sometimes difficult to achieve in a casting system.

The W-Mo thermocouple was first used in this work. This thermocouple passes through a minimum at 675°C , changes polarity at 1325°C , and has a very large temperature coefficient. Thus in the region of interest the slope is about 120°C per millivolt. A thermocouple made of W-Nb, however, has a much more favorable coefficient, about 65°C per millivolt. Consequently this couple has been adopted for the casting of thorium.

2.3 Shielding of Thermocouples. The zinc vapor that was produced when the zinc was boiled out at 900 to 1300°C condensed on the thermocouples and caused the shorting out of the couple. For this reason virtually gastight shielding was required on the couple to the point of exit from the vacuum chamber. Besides such shielding, the usual insulation of the couple wires from each other was required. None of the commercial products, available for the latter purpose, made of alundum or similar refractories could withstand the temperature required. Hence it was necessary to fabricate special high-temperature insulators and shields for this use. Beryllia had proved to be the most refractory and at the same time most strong mechanically and most resistant thermally of the available refractories. Hence two-holed BeO thermocouple insulation was formed by fastening paraffined cotton cords in position in a hollow cylindrical graphite form, jolting BeO into the tubular space around the cords, and firing the body in the induction furnace.¹² In this procedure the cord was burned out as the insulator was sintered. The shields were formed by the usual jolting and firing process for forming crucibles.⁸ The shields thus produced were fitted with stepped ends for inserting into each other in such fashion that a number of 8-in. lengths could be built into a very tight tube of any desired length.

To protect further the thermocouples, shields, insulation, and other parts of the system from the zinc distillate, K-30 firebricks were shaped (by sawing, drilling, and buffing) to fit around the thermocouple shields and into the upper portion of the vacuum chamber. These bricks acted as condensers which absorbed a large amount of the zinc condensate.

3. PRESSURES OBTAINED DURING CASTING IN VACUO

Thorium has thus far been cast in vacuo although some remelting of Th-Zn alloy at lower temperatures (1200°C) has been done under argon. Various pumping systems have been employed, depending on

the scale of operation or the equipment available at the time.

3.1 Vacuum Equipment. Castings have been made with such equipment as was available at the time of producing the required metal. Cenco Hypervacs, mercury diffusion pumps backed by Cenco Hypervacs, and an oil diffusion pump backed by a Kinney pump have been used for different castings. The system now in use consists of a Model B-8-O four-stage oil diffusion pump built by the National Research Corp., with a 100-cfm Model DVD 8810 Kinney mechanical pump used as the fore pump. The system has a capacity of 1200 cfm. A McLeod gauge in the line adjacent to the vacuum chamber was used to measure the pressures recorded.

3.2 Zinc Pressure during Casting in Vacuo. Considerable pressures are developed during the remelting and casting of the Th-Zn alloy in vacuo. A typical curve of the changes of pressure with temperature and with time is presented in Fig. 1. It will be seen that the pressure rises during the early heating up to about 700°C, rises less rapidly to a maximum at 900°C, continues with slight decrease to about 1100°C, decreases more rapidly to 1600°C, and starts to rise again from 1700 to 1800°C. If the temperature is permitted to rise much above 1800°C a marked rise from 1800 to 1900°C occurs. The first of these rises (25 to 600°C) marks the degassing of the system. The second increase, from 600°C and the maximum maintained from 1000 to 1200°C, marks the distillation in vacuo of the zinc from the alloy. The greater portion of the zinc is removed during this temperature interval, especially if the temperature is held in this interval from 20 to 30 min, according to the size of the charge. The decrease of pressure from 1200 to 1600°C marks the completion of the removal of zinc and the restoration of vacuum obtainable by the system.

During the dezincing in vacuo the metal becomes plastic and becomes deformed to some extent. It does not flow freely, however, to assume the shape of the vessel. It is left in a spongy state with blowholes throughout. If the dezincing is done slowly, 20 to 30 min being used in raising the temperature gradually from 800 to 1200°C, the metal changes shape very little. If the metal is heated too rapidly during this period the zinc boils out explosively, and metal is blown from the crucible and mold. The zinc pressure decreases from 900 to 1600°C, and at that point only about 200 ppm of zinc remains in the thorium.

3.3 Beryllium Pressure. On approaching 1800°C a second increase in pressure usually occurs (Fig. 1), especially if the temperature is permitted to approach 1900°C. In such cases the beryllia melting crucibles may be deeply eroded, amounting to as much as

$\frac{1}{16}$ in. The billet of thorium obtained in such a case is covered with a greenish-brown glaze containing oxide and metal. The increase of pressure and erosion of the beryllia indicate that the reduction of beryllia by thorium is proceeding owing to the volatility of the beryllium thus produced.

3.4 Melting of Alloy under Argon. It is possible to melt the alloy in an inert gas, such as argon, at atmospheric pressure. Under these conditions the alloy melts at about 1200°C and flows freely to assume the shape of the vessel. This procedure is very useful in shaping the crude alloy for casting by self-induction and for other purposes, as will be pointed out later.

4. METHODS OF HEATING

The charge of metal being melted or cast may be heated either by a graphite heater or by self-induction. Melting by self-induction requires good inductive coupling (and insulation) for reasonable speed of heating. Since the size of the mass being melted cannot always be easily adapted to the heating equipment available (the size is determined somewhat by the scale of reduction), heating by self-induction is not always desirable or even possible in some cases. Most of the casting to date has been done by the use of graphite heaters.

Graphite Induction Heater. The graphite heaters are machined from cylinders of graphite. In some cases the same heater extends over both crucible and mold, and in other cases separate heaters are made for the two for the purpose of obtaining different crucible and mold temperatures.

The use of cold molds has not been possible with thorium owing to its high melting point. Premature freezing, producing voids and cold shuts, results from a mold that is too cold. Successful casts of cylinders have been made with the mold at temperatures as low as 1600°C in an effort to minimize reaction of the thorium with the mold material. Usually the mold is kept at virtually the same temperature as the crucible.

5. INSULATION

The insulation of the heater and charge is much more difficult at higher temperatures than at the lower ones at which most metals melt. Insulation in an induction-heated vacuum casting system may be achieved by metal reflectors, by refractory shields which act both as insulators and as reflectors, and by loose packing. The use of metal reflectors has not been sufficiently experimented with on the scale of 100 to 200 lb at 1800°C to conclude finally as to its efficiency.

However, sufficiently refractory metals are not readily available in quantity, and this procedure has not been employed.

5.1 Refractory Shields. The use of refractory shields concentrically arranged around the crucible or heater is very satisfactory up to temperatures of 1400°C or even 1500°C. In the casting of uranium a double shield of sillimanite supplies adequate insulation for the melting of uranium at 1250°C. However, at 1800°C sillimanite could not be used next to the heater, nor would two layers of refractory supply sufficient insulation.

A three-layered system of shields was used in one casting of a 70-lb charge in the large 15-in. coil (B, C, and D of Fig. 3). Of the refractories available, only lime, magnesia, or beryllia can be used adjacent to the graphite heater, whose temperature may reach 1850 to 1900°C. The commercial alundum and sillimanite both melt below this temperature. Since magnesia had been fabricated into mechanically and thermally strong bodies by a wet-jolting method,⁸ it was selected for the fabrication of the inner shield. Alundum formed by plastic casting was selected for the intermediate shield, and sillimanite also formed by plastic casting was chosen for the outer shield. These shields were, respectively, 10, 11, and 13 in. in O.D. This insulation proved adequate in quantity, and the casting was successfully completed. The various shields touched in spots, however, and in these spots complete fusion occurred owing to the lowering of the melting points of the mixtures. As a result of the mechanical difficulties of fabrication of uniform wares (shrinkage on firing was not consistent), it was apparent that the use of fired shields with such close tolerance as to avoid contact would be very difficult and that further efforts along this line would not be profitable.

5.2 Loose-packed Refractory. In view of the additional delay and the expense involved in the above procedures, the more certain procedure of loose-powdered refractory between shields, or between a shield and the quartz vacuum envelope, was employed. Carbon black was investigated, but it produced so much carburization of the metal owing to its being blown about in the chamber during degassing, etc., that its use was abandoned. Magnesia was successfully employed but could not be used in contact with the graphite heater. Hence magnesia shields were built with a space of about $\frac{1}{4}$ in. between heater and shield. The space between the shield and a second outer concentric shield was then filled with 200- to 300-mesh high-calcined magnesia. In some cases no outer shield was necessary, and the space between the inner shield and quartz vacuum envelope was filled with magnesia. Some of the magnesia had a boron content (20 to 100 ppm), and for this reason beryllia was similarly used in some situ-

ations. Such a pack of loose insulation requires a minimum of fabrication, and in experimental casts, or casts for a single object which will not be repeated, the saving of time on ceramic fabrication is very desirable.

6. SPECIAL SHAPES AND SIZES

Since the study of thorium is still in the experimental stage a large number of different shapes of various sizes have been required by various chemical, physical, and metallurgical investigators. Usually only a few pieces of the same size and shape were desired. Hence the details of the construction of the casting equipment have varied from job to job to such an extent that a description of all of them would not be profitable. From the following descriptions of a few typical castings and from the general principles outlined above the conditions used in other cases could be reduced.

6.1 Cylinders. A number of cylinders of various sizes have been required for the investigation of the extrusion of thorium. Cylinders 2 in. in diameter and 4 in. long were typical of this shape. These cylinders were cast in vacuo by melting the Th-Zn alloy in beryllia crucible F and permitting the molten metal to flow through a 1¼-in. orifice in the bottom of the crucible into a beryllia mold H as shown in Fig. 2. No valve was used in controlling the flow of metal. The crucible and mold were heated by a graphite heater E. Temperature was measured by the W-Nb thermocouples A, J arranged to measure the temperature near the bottom of the charge and in the heater near the top of the mold. The heater was insulated by a shield D of MgO or BeO surrounded by a loose packing extending from the insulation shield to the quartz tube B. In other cases it was more convenient to set up the melting equipment on the water-cooled head and slip the vacuum jacket over the assembly. In this case it was necessary to use two shields, the outer shield of sillimanite, and place the loose packing between the two.

The vacuum chamber consisted of a fused-quartz envelope B, about 9½ in. I.D., closed by a brass water-cooled vacuum head with a flange finished on its inner surface. A tight fit between the flanged surface and the ground end of the quartz tube was secured by a rubber gasket greased with Lubriseal. The vacuum head was equipped with leads for the cooling water and outlets for the thermocouples.

A charge of the size required for a 2-in.-diameter cylinder (about 7 lb) requires about 70 to 75 min of heating. Heated at 25 kva for 10 min the temperature rises rapidly to about 600°C, more gradually to 900°C, levels off while the major portion of the zinc is being boiled out, rises to about 1200°C in 25 min more, again increases in rate

of rise to about 1600°C, and gradually decreases in rate of rise again during the final heat from 1600 to 1800°C (Fig. 1).

It is necessary to heat slowly during the interval from 900 to 1200°C, or the sudden evolution of zinc may sometimes blow a considerable portion of the charge from the melting crucible and cause damage to the equipment or interfere with the thermocouples. This operation usually requires 20 to 25 min during which time the power is decreased to 18 kva if necessary.

Charges of 6 to 20 lb into 2-in. cylinders, 3- to 4-in. disks, or rectangular shapes have been cast under approximately the above conditions.

6.2 Hemispheres. A thorium sphere 8 cm in radius was required. It was decided to cast the sphere in halves, machine each hemisphere, and surface grind the flat faces. For this purpose it was necessary to cast each hemisphere with a cylindrical top 1 to 1½ in. longer than the radius of the sphere to facilitate chucking on the lathe. This required a charge of about 70 lb of Th-Zn alloy. The apparatus used for this casting is shown in Fig. 3. A beryllia crucible F was used for the melting, with a hole about 1½ in. in diameter for the flow of metal into the mold H. The beryllia mold, 17 cm I.D., with a hemispherical bottom was formed by jolting on a pneumatic jolter into a graphite form with a cylindrical graphite mandrel with a hemispherical base. This beryllia mold was fired in the induction furnace at 1850°C.

The charge was heated by graphite induction heaters E, I surrounded by the three-shield insulation system of magnesia D, alumina C, and sillimanite B, described in Sec. 5.1. W-Nb thermocouples were placed in wells G and L. A power rate of 38 to 40 kva is required for 60- to 100-lb charges of thorium with the above insulation in the 15-in. coil heated by the 70-kva Ajax Electrothermic Corp. converter. With such heating the temperature rises at about 30°C per minute to 600°C, 25°C per minute to 800°C, 12°C per minute to 900°C, 8°C per minute to 1300°C, and then increases to 12°C per minute for the next hundred degrees after which it gradually falls off to 6°C per minute at 1800°C owing to increasing heat loss with higher temperature differential. A period of 2½ hr is required to heat a charge of 60 to 100 lb of thorium to 1800°C in the above system. After reaching 1800°C the temperature was held at that point for 30 min with a power of 30 kva.

6.3 Melting in Situ. The melting of crude Th-Zn alloy in situ without any flow from one vessel to another has been used in a number of cases. In this procedure the adherent slag and oxide film float to the top of the molten charge, and sound castings are obtained. Owing to the high viscosity of the metal at 1800°C, flow through orifices smaller than 1 in. is very difficult; hence casting into small diameters

by pouring is uncertain. A number of 1.1-in. cylinders 4 in. long were formed by melting the alloy in beryllia molds (1¼ in. I.D.) without pouring and by machining the resultant bodies to the desired dimensions. The crude metal was shaped to fit into the molds by reducing in 4-in. bombs with constricted lower sections 1 in. in diameter or by melting the alloy under argon at a pressure of 1 atm at 1200°C and pouring into graphite molds 1 in. in diameter. In this process no reaction occurs with graphite at this temperature.

7. COMPOSITION AND PURITY

7.1 Composition. The thorium metal produced by the above procedures has contained from 2 to 6 per cent of combined thorium as oxide or carbide or both. The carbon content of the metal cast by the use of graphite heaters has varied from 0.02 to 0.25 per cent (usually from 0.07 to 0.12 per cent), representing 1.5 to 2.5 per cent thorium monocarbide. The combined thorium as oxide constituted 0.5 to 3 per cent (usually 1.5 per cent) of the total. Thus, on the average, 3 per cent of the thorium was combined as oxides or carbide. Elements other than thorium constituted about 0.6 per cent, leaving about 96.5 per cent of the cast mass as free thorium metal with a total thorium content of 99.4 per cent. Owing to the reaction with the refractory and with the atmosphere of the casting system and owing to the use of impure raw materials, the thorium content in some cases ran as low as 96 per cent.

7.2 Purity. Besides the major components listed above, other impurities were found in the cast thorium either from the crude metal, the refractory, or the atmosphere. Beryllium from the crucible constituted the major metallic impurity, with carbon, oxygen, and nitrogen the major nonmetallic impurities.

The upper and lower limits of these impurities and the usual composition are presented in Table 1.

The reaction of thorium with the oxide refractories on melting introduced considerable oxide (1 to 3 per cent) into the cast metal. Carbon volatilized from the graphite heater was present in sufficient quantity to produce 1 to 3 per cent of carbide. As a result 1 to 6 per cent of combined thorium may be present under operating conditions to date. From 0.06 to 0.2 per cent Be is also picked up from the crucible. The investigation of other refractories and the improvement of vacuum techniques are under way to decrease these reactions.

The composition of the metal with respect to thorium and major impurities is presented in Table 2.

The carbide and the oxide of thorium occur in the metal both as grain boundary and as intragranular inclusions. These inclusions

chip when machined and darken when permitted to stand. Improvement of vacuum has not been as effective as careful control of temperature in the elimination of inclusions. Improvement of the vacuum from several hundred μ Hg to 1 μ Hg failed to improve the metal at temperatures of 1900°C, while careful control of temperature not to exceed 1800°C resulted in much cleaner metal although the pressure was 100 to 300 μ Hg.

8. SOME PHYSICAL AND METALLURGICAL PROPERTIES OF CAST THORIUM

The complete treatment of the physical and metallurgical properties of thorium does not constitute a part of this paper. However, some of the properties investigated in the solution of the casting problem and some of the properties involved in the uses of the product should be considered here.

8.1 Density. The cast thorium has varied in density from 11.25 to 11.5 g/cc, varying with the amount of included material (oxide, carbide, slag). The density of the greater portion of the cast metal has been 11.48 g/cc, measured by immersion methods. X-ray determinations of lattice spacing have shown densities as high as 11.64 g/cc for some of the cleaner metal. The density of the pure element is probably as high as 11.7 g/cc.

8.2 Hardness. The hardness of the cast metal varies from 60 to 80 on the Rockwell E scale, depending on the quantity and nature of the inclusions. This would indicate that the pure element has a hardness lower than 60 Re, probably considerably lower. When the metal is cold-rolled, the hardness is considerably increased, approaching 95 Re as a limit. This is true regardless of the original hardness.

8.3 Machining and Grinding. Cast thorium can be readily sawed with Marvel tool-steel edged blades with or without coolant. It is easily machined with high-speed tools at speeds of 150 to 175 rpm on the 4¼-in. billet, or about 160 to 190 ft/min. Surface grinding produces a smooth highly reflecting surface which darkens on standing in air in proportion to the amount of included material.

8.4 Rolling.¹³ The cast metal does not cold-roll well; edge cracking occurs up to 30 per cent reduction and is not healed on further reduction. Only 50 per cent of the metal was usable after 80 per cent reduction. On hot-rolling, however, much less edge cracking occurred, and 90 to 95 per cent of the metal was usable after 80 per cent reduction. At 800°C some edge cracking occurred, but 90 per cent of the metal was usable, while at 900°C only very slight edge cracking occurred; and on 80 per cent reduction 95 per cent of the metal was usable.

8.5 Extrusion.¹⁴ Two-inch-diameter billets of cast thorium were easily extruded at about 800°C at a pressure of 43 to 57 tons/sq in. Standard 4¼-in. billets were in preparation for extrusion at the time of writing.

9. IMPROVEMENT OF CASTING OF THORIUM

Further work is in process in the improvement of the quality of thorium metal by: (1) improving the vacuum; (2) more accurate determination of optimum temperature and more accurate temperature control; and (3) further investigation of allowable ceramic materials.

Table 1 — Purity of Cast Thorium Metal Made from Column-purified Salt

Impurity	Lower limit, ppm	Upper limit, ppm	Usual content, ppm
C	500	2000	1200
N	200	800	350
Al	100	700	300
Si	100	700	300
Zn	<5	100	<5
Fe	40	125	
Ca		<25	
Mg		<30	
Ba		<25	
Na	5	15	
Mn	1	7	3
Pb		<5	
K	5	10	
Li		<2	
B	0.3	1.5	<0.5
Cd		<0.2	<0.2
U		0.2	<0.2

Table 2 — Major Components of Cast Thorium Metal

	Lower limit, %	Upper limit, %	Usual, %
Thorium, free	94	99	96.5
Thorium, combined	1	6	2
Thorium, total	95	99.5	99.4
Beryllium	0.02	0.08	0.06
Nitrogen	0.02	0.08	0.035
Carbon	0.05	0.2	0.12

Fig. 1 — Typical curve of the changes of pressure and temperature with time.

Fig. 2—Cylinder casting apparatus.

(A) W-Nb thermocouple	(E) Graphite heater
(B) Quartz tube	(F) Beryllia crucible
(C) Port to facilitate re-
moval of zinc vapor	(G) Loose packing
(D) Shield	(H) Beryllia mold
	(J) W-Nb thermocouple

Fig. 3 — Hemisphere casting apparatus.

(A) Vacuum chamber	(G) Thermocouple well
(B) Sillimanite shield	(H) Beryllia mold
(C) Alumina shield	(I) Graphite induction heater
(D) Magnesia shield	(J) Magnesia insulating plates
(E) Graphite induction heater	(K) Support plate
(F) Beryllia crucible	(L) Thermocouple well

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Paper 8.6

A PILOT PLANT FOR PURIFICATION OF THORIUM NITRATE BY COUNTERCURRENT EXTRACTION

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ABSTRACT

A continuous countercurrent liquid-liquid extraction system has been constructed for the purification of thorium nitrate. The thorium feed solution is 3M in calcium nitrate, 3M in nitric acid, and 0.445M in thorium nitrate. Methyl isobutyl ketone is used as the extracting agent. The extraction column is 3-in. pyrex-glass pipe packed with Berl saddles. The optimum extraction was obtained with the following flow rates of column solutions: feed solution, 7 to 8 gph; scrubbing solution, 1 gph; hexone, 15 gph; water, 3 gph. The extraction column has operated satisfactorily to give consistently at least 99.7 per cent recovery of thorium, but the exact separation factors from the impurities in the thorium nitrate are not known.

1. INTRODUCTION

Exploratory work¹ on the extraction of thorium nitrate with organic solvents indicated that the process would give a product sufficiently pure for nucleonic purposes.

A continuous countercurrent liquid-liquid extraction system was constructed for the purification of large quantities of thorium nitrate. Based on the preliminary work previously reported,¹ the extraction column was designed to operate with a nitric acid solution of thorium nitrate containing a salting-out agent and with hexone as the organic solvent.

2. DESIGN AND CONSTRUCTION OF THE EXTRACTION SYSTEM

The extraction system is housed in an enclosed stairwell extending 65 ft from the basement to the roof of the building. There is a working area 9 by 6 ft with steel-grating platforms at the building floor levels (see Fig. 1). The basement area is larger, 9 by 10 ft, with a concrete floor sloping toward a drain in the center which allows the column to be readily washed down. An adjoining room on the fourth floor is used for the calcium nitrate recovery system and for the make-up tanks.

To prevent arcing which might cause an explosion should the concentration of hexone vapor be too great and to protect the installations from the corrosive solutions used, all wiring in the lower part of the shaft is run through a conduit into explosion-proof and waterproof motors, lights, and switches. One of the large exhaust fans in the building provides ventilation for the shaft. Each level is equipped with two showers, one inside the shaft and one outside, readily accessible in case of accident. In addition to these safety precautions, a master switch located outside the shaft at the top floor permits shutting off the entire electrical system without entering the shaft. Stopping the pumps will automatically shut down the operation of the columns after a short interval.

The system includes two columns: a hexone extraction column in which thorium nitrate is extracted from the feed solution by hexone, hereafter to be referred to as column 1; and a water extraction column which reextracts the thorium nitrate from the enriched hexone with distilled water, hereafter to be referred to as column 2.

It was estimated that a 26-ft hexone extraction column and an 18-ft water extraction column would be sufficient for complete extraction and reextraction. Each of these columns is made up of 6-ft lengths of 3-in. I.D. standard flared pyrex-glass pipe. Column 1 consists of four 6-ft lengths and two 1-ft tees, one tee 6 ft from the top for feed, the second 6 ft from the bottom as an extra inlet to inject nitric acid if necessary (see Figs. 1 and 2). Column 2 is made up of three 6-ft lengths.

Each section of the pyrex pipe contains about 13 lb of $\frac{1}{2}$ -in. unglazed porcelain Berl saddle packing. These saddles are supported at the bottom of each section by a piece of $\frac{1}{4}$ -in. stainless steel screen woven into the shape of a paraboloid of revolution (see Fig. 2). Each 6-ft section weighs 11.9 lb, and when filled with column solutions each section has a total weight of 41 lb. Polyfluoethylene $\frac{1}{8}$ in. in thickness was found to be very satisfactory as gasket material between sections

since it resisted both the nitric acid and organic solvents used in the columns.

Two 3-in. angle irons running the height of the shaft form the framework for the supports of the pyrex pipe column. The columns are supported on spring mounts, a pair of springs at each joint between sections of the pyrex pipe (see Fig. 3). The mounts are supported on horizontal 1½-in. angle-iron arms bolted to the framework. The spring-type mount and the support of the Berl saddle packing make it possible to remove each section independently in case of breakage. The disposition of tanks, pumps, and the two columns is shown in Fig. 1.

The scrubbing solution enters at the top of column 1, the feed solution enters through a 1-ft pyrex tee 6 ft below the top of column 1, and the hexone enters at the bottom of the column (see Fig. 2). Hexone is made the dispersed phase in both of the columns because a better degree of dispersion is obtained than when the aqueous phase is made the discontinuous phase. There is also less hazard with hexone as the dispersed phase in the columns. The enriched hexone leaves the top of column 1 where it overflows into an open reservoir. From this reservoir it flows into the bottom of column 2 where it rises through distilled water which reextracts the thorium nitrate. The raffinate flows out of the bottom of column 1 up through an interface leveling system (see Fig. 4) and down into the raffinate storage tank. The product solution from column 2 comes out at the bottom, likewise passing through a leveling device and down into the product storage tank.

The interface leveling devices control the height of the interface between the organic layer and the aqueous layer of the columns by varying the height of the raffinate or product overflow lines. The levels of the interfaces are fixed by the rates of flow of the various solutions into and out of the columns. It was found that the adjustment of an interface to a desired point required a more delicate control than was possible with the type valve available. In addition to discharge lines connected directly to the raffinate and product tanks, inverted U loops were installed. These loops, which can be raised or lowered, include overflows. They are installed so that they bypass the outlet control valves and provide a fine adjustment, whereas the outlet valves provide the coarse adjustment. A small variation in height of the overflow results in a corresponding movement of the interface in the column. This movement is controlled by a sliding vertical rod attached to the overflow and extending to the control platform on the second floor.

The inverted U is given the necessary freedom of movement up and down by inserting a helix of ⅜-in. Saran tubing on the column side and by having the outlet side flow into a 3-ft length of 1-in. pipe in

which the $\frac{1}{4}$ -in. pipe can slide freely. The helix is about 6 in. in diameter and has an over-all extension of about 3 ft, with corresponding effect upon the position of the interface. The depleted hexone is forced out of the top of column 2 and into the storage tank from where it is recycled.

All column liquids are fed to the column from constant-head tanks. The hexone constant-head tank is 56 ft above the bottom of the first extraction column. This is necessary because the head of hexone (specific gravity = 0.80) must balance the head of the liquid in the column (average specific gravity is approximately 1.4). Feed under gravity head, using head tanks with overflows to maintain constant levels of liquid in the lines to the columns, was chosen instead of pumping the solutions directly into the columns. This method ensures steady rates of flow in all liquids entering the columns. The necessary head room for such an arrangement was available.

The flow rates of feed solution, scrubbing solution, hexone, and distilled water are indicated by Schutte & Koerting Co. rotameters and are regulated from a panel on the second floor of the shaft (see Fig. 5).

All storage tanks, constant-head tanks, pipe, fittings, and valves are of 18-8 type-304 stainless steel. The feed and scrubbing solutions are made up and stored in 100-gal tanks at the top of the shaft and are piped down to the 50-gal tanks on the second floor that supply the pumps (see Fig. 1). These pumps which supply the solutions to the 4-gal constant-head tanks are single-stage centrifugal pumps of stainless steel (Eastern Engineering Div., Eastern Industries, Inc.). Hexone is pumped from its 50-gal storage tank to the constant-head tank by a triple-stage centrifugal pump. The flow rates to the constant-head tanks are adjusted by stainless steel gate valves and are regulated so that a small stream of liquid is constantly returning from the overflow. Stainless steel screen (200 mesh) at various points in the lines removes foreign matter from the solutions. All the piping is $\frac{1}{4}$ in. except the overflow lines from the constant-head tanks, which are $\frac{3}{8}$ in. Drains were installed at the bottom of each column (see Fig. 6).

The raffinate from column 1 is collected in a 50-gal tank on the first floor. This tank is equipped with a mechanical mixer as an aid in neutralization. The product solution from column 2 is collected in one of three 50-gal tanks, each equipped with a stirrer (see Fig. 7).

3. CALCIUM NITRATE RECOVERY SYSTEM

The raffinate from column 1 under steady-state conditions during production runs is collected in a 50-gal tank on the first floor. It contains the following constituents in these approximate concentrations:

calcium nitrate, 3.75M; nitric acid, 0.15M; unextracted thorium nitrate, 0.01M; the rare earth nitrates in unknown amounts; most of the other undesirable metal nitrates; and possibly some of the products of the reaction between hexone and nitric acid.

The raffinate is neutralized by the addition of screened lime with constant stirring by a mixer, which precipitates thorium and rare earth hydroxides. To this magma is added a filter aid (The Dicalite Company, Speedex grade), 6 lb to 40 gal, to facilitate filtering. This slurry is stirred and fed by gravity to a 30-gal montejus in the basement below. Using air at 70 psi and a system of valves, the slurry is forced out of the montejus and up 60 ft into storage tanks at the top of the shaft. From these storage tanks, the slurry is fed by gravity into a 45-gal montejus connected to a standard 8-in. (Sweetland Waste Co.) leaf-type filter using No. 145CH Filter-Media filter cloth.

The slurry is forced by air at 70 psi through the Sweetland filter and into storage tanks at the rate of 25 gph (see Fig. 8). This solution has a specific gravity of approximately 1.42 (varying under different column conditions) and contains 7.5 lb of calcium nitrate tetrahydrate per gallon. The filter cake containing the thorium hydroxide and rare earth hydroxides is stored in barrels for future recovery of the thorium.

A part of the calcium nitrate solution is concentrated in a steam evaporator to a boiling point of 132°C which is the boiling point of calcium nitrate tetrahydrate. This salt is drawn off in the molten state (melting point = 42°C) and is poured directly into the make-up tanks. Using calculated portions of molten salt and the calcium nitrate solution of density 1.42, it is possible to make up the feed and scrubbing solutions to the desired density without the addition of water (see Sec. 4.1).

All the apparatus of this recovery system, with the exception of the raffinate collecting tank and stirrer which are stainless steel, is of ordinary iron pipe or cast iron. The montejus are of 12-in. iron pipe with top and bottom welded on. All piping is ½-in. black iron. Since the solution is slightly alkaline, the type of material is not critical so the cheapest or most available material is used.

The lime is screened while being added to the raffinate to prevent the formation of large lumps. If this is not done, the chunks of slaked lime plug up the ½-in. lines in the system.

4. OPERATION OF EXTRACTION SYSTEM

The operation of the extraction system can be briefly described as follows: Hexone is passed into the bottom of the first extraction column and allowed to rise through the scrubbing solution and thorium feed solution which are admitted at the upper section of the column.

The interface between the aqueous phase and the enriched hexone phase is kept about a foot from the top; enriched hexone continually overflows and enters the bottom of column 2. Here distilled water, entering at the top, washes it free of thorium and nitric acid. The technical operations involve making up the column solutions and analysis of solutions. These techniques and the results of experimental runs are described in detail in the following discussion.

4.1 Preparation of Column Solutions. The feed and scrubbing solutions are made up in 100-gal stainless steel tanks according to the specifications given in Table 1. These give final compositions of 3M nitric acid and 3M calcium nitrate for both feed and scrubbing solution; in addition the feed solution is 0.445M in thorium nitrate tetrahydrate. About 4 hr of vigorous stirring is required to get the solid salts in solution. The final specific gravities should be 1.435 and 1.59, respectively, for scrubbing solution and feed solution. The final specific gravities of the solutions are determined by hydrometers as a check on the composition.

After a sufficient amount of calcium nitrate has been recovered (see Sec. 3), it is used in the feed and scrub make-ups in place of commercial salt.

The recovered calcium nitrate solution has a specific gravity of about 1.42. In using it to make up feed and scrubbing solutions, part of the calcium nitrate is added directly as the recovered solution, and the rest is evaporated to 132°C (the boiling point of calcium nitrate tetrahydrate) and added directly as molten salt. These amounts can be readily calculated and are given in Table 1. Addition of molten salt instead of solid calcium nitrate tetrahydrate has the advantage of cutting down the time required for dissolving to about 1 hr.

4.2 Techniques of Operation of Extraction System. The 50-gal tanks for feed, scrubbing solution, and hexone are filled by gravity through 200-mesh stainless steel screen sediment filters. The pumps below these tanks are turned on, and the liquids are pumped to the constant-head tanks for each. The distilled water is added directly to its constant-head tank from the distilled-water line. The flows of the three pumped liquids are adjusted by gate valves in the line so that there is an overflow from the constant-head tank to the storage tank; in the case of distilled water, a faucet is adjusted to give an overflow.

When the constant-head tanks are filled, the volumes of scrubbing solution and feed solution in the 50-gal storage tanks are measured by a calibrated measuring stick. When the columns are empty initially, column 1 is filled three-fourths full of scrubbing solution and column 2, three-fourths full of distilled water. At this time feed and hexone are introduced, and their flows are adjusted by means of needle valves to the desired rotameter readings.

At the start the interface regulators are lowered; when the columns are filled, a coarse adjustment of the interface is made with the bypass valve, and then a fine adjustment is made from time to time with the interface regulators to keep the interfaces near the top of the Berl saddle packing (about 1 ft from the top of the column).

When the columns have been left filled from a previous operation, the feed and hexone flows can be started immediately upon filling the tanks as before. It is advisable to increase gradually the flow rates to the desired values in order to keep the interface within the column. Again the interface regulators are kept at the lowest points at the start of column operation, and the bypass valve is opened to adjust the column interface.

When the column is being operated, a steady state is reached in about 1 hr. After this time only minor adjustments of the interface regulators are required if the flow rates are kept constant.

During experimental runs, samples of hexone, raffinate, and product are taken when a steady state is reached. During production runs the analysis of thorium in each product tank is taken after the tank is filled. Thorium in the raffinate is checked from time to time by noting the precipitate formed when ammonia is added; usually the solution remains clear or shows only a faint cloudiness.

Under the conditions of column operation during production runs (feed solution, 7.5 gph; hexone, 15 gph; scrub solution, 1 gph; water, 3 gph), the product tanks become filled in about 8 hr of operation. The product outlet is shifted to another tank when one becomes filled. After analysis, the proper amount of oxalic acid is added to precipitate thorium oxalate. The thorium oxalate is washed thoroughly with water, centrifuged, dried, and then calcined at 650°C to form thorium dioxide. The oxide is hydrofluorinated, and the resulting fluoride is reduced to thorium metal. These precipitations and reduction processes are fully described in other reports.²⁻⁴

When the raffinate tank is filled, lime is added to neutralize the acid and precipitate thorium and rare earths present, and the slurry is sent through the calcium nitrate recovery system (see Sec. 3).

During operation the pumps must be checked for leakage from time to time since the solutions are all very corrosive. To minimize leakage due to attack on the pump packing, an alternate procedure of column operation has been to fill the constant-head tanks intermittently and shut off the pumps until the tanks need to be refilled. The slight change in rate of flow due to the diminishing head of liquid can be taken care of by readjusting the control valve.

In discontinuing column operation either at the end of a day's run or, in continuous operation, for repairs, the usual procedure is as

follows: Hexone and feed valves are shut off, and the column is allowed to stand until all the hexone has risen to the top of the column; then the flow rate of scrubbing solution is increased, which causes the hexone to be forced out the top of column 1. The scrubbing solution is then shut off. It is essential to remove all the hexone since a reaction occurs when hexone is left in contact with feed or scrubbing solution. As soon as all the hexone has risen to the top of column 2, the distilled water is shut off, and the solution in column 2 is drained into the product tanks.

4.3 Calibration of Rotameters. Two methods were used to check the rotameter calibration charts supplied by the manufacturers. The first was to weigh the feed solution, scrub solution, water, or hexone running from the constant-head tanks through the rotameters at a given scale reading during a short time interval. Knowing the specific gravity of solution, the rate of flow could be calculated. The other method was to drain down the full constant-head tanks, of which the volumes were previously determined, at a given scale reading of the rotameters and to note the total time required.

The operation of the column was tested without feed solution, i.e., using only scrubbing solution, hexone, and distilled water. This run showed that the interface regulators were near the correct height and that all pumps and valves operated properly.

4.4 Experimental Runs and Optimum Extraction Conditions. In the experimental runs described below, the flow rates of feed solution, scrubbing solution, hexone, and water were varied systematically to determine the operating conditions which would give maximum thorium extraction.

The data obtained during the experimental runs are given in Table 2. The first run gave a product solution which was too dilute, and there was considerable thorium in the raffinate, but the hexone was completely stripped of nitric acid. The experiments following this were designed to find the conditions that would remove all thorium from the raffinate and give a product solution sufficiently concentrated in thorium without leaving too much nitric acid in the hexone.

During the first three runs there was considerable variation of the position of the column interfaces because the techniques of adjusting the interface regulators had not been worked out.

Runs 4, 5, and 6 were made successively in 1 day with the same feed solution for the purpose of demonstrating the effect of variation of the hexone-to-feed ratio. The diminishing of the extraction as this ratio decreased below 2 is very clearly shown. This, coupled with data from other runs which are shown in Table 3, indicates that the optimum hexone-to-feed ratio is between 2 and 2.5. However, there is

some variation in the amount of scrubbing solution used in these runs, and this may influence the over-all extraction of thorium. The amount the extraction is decreased by the increase of scrubbing solution is shown in Table 4. The effect of scrubbing solution could be due to the dilution of feed solution in the column and to a reextraction of thorium from hexone in the scrubbing section of the column.

The time allowed for a steady state to be reached, after which samples were taken for analyses, was 2 hr in all cases. A test in which samples were taken after 2 hr and after 2½ hr of operation gave results identical within experimental error, thus verifying that the steady-state conditions were reached after 2 hr.

Remarks on Experimental Runs.

Runs 1, 2, 3: Mechanical difficulties were encountered in operation; interface heights varied widely.

Runs 4, 5, 6: Approximately 2 hr was allowed for equilibrium. Hexone-to-feed ratio varied from 1.75 to 0.7.

Run 7: Operating conditions were good.

Run 8: Tried to reach flow rates of 7½ gph for feed and 22 gph for hexone. Violent reaction occurred during run.

Run 9: Operating conditions were good, but calcium was detected in product.

Run 10: Dispersed interface, difficult to control column interface positions.

Runs 11, 12, 13: Continuous difficulty with interface as in Run 10. Calcium in product 0.1M to 0.3M.

Run 14: Feed was introduced at top of column where the scrubbing solution was usually introduced (no scrub used).

Run 15: No scrubbing solution was used; no calcium in product solution.

Run 16: Feed rate was variable; no data were taken.

Run 17: Satisfactory run; extraction of thorium decreased toward end of run.

Runs 18, 19, 20: Production runs; no equilibrium data were taken.

Run 21: Hexone was green colored; it was therefore less efficient in extraction.

The data taken during a run are illustrated by the example of Run 7 given in Table 5 and the following data.

Flow rates: Feed solution, 7.75 gph; scrubbing solution, 1.5 gph; hexone, 16 gph; water, 2.5 gph.

Equilibrium samples: Raffinate was collected at a rate of 500 ml/min and when analyzed gave 0.04 g of TNT per 100 ml. Product was collected at a rate of 235 ml/min and when analyzed gave 53.9 g of TNT per 100 ml. Calculation gives a 98.5 per cent extraction of tho-

rium. Contrary to most runs, the hexone contained 0.49 g of TNT per 100 ml.

Material balance: Thorium in with the feed, 29.12 lb. Thorium out: with product, 28.3; with raffinate, 0.46; with hexone, 0.24: total out, 29.03 lb. The net loss is 0.097, which is within the error of the quantity measurements.

The data obtained by Run 9 had indicated the optimum conditions. Before a given set of conditions for production runs was decided on, a few more experimental runs were made. In these experiments an additional difficulty, the lack of rapid separation of interfaces, was encountered; this is discussed in Sec. 4.6. This difficulty still has not been solved, but additional experiments showed that satisfactory extraction could be obtained in spite of it. The following data are from a typical production run.

Flow rates: Feed solution, $7\frac{1}{2}$ gph; hexone, 15 gph; distilled water, 3 gph. The product was collected at a rate of 5 gph; the raffinate was collected at a rate of 7 gph.

Product: The product contained 1.4 lb of Th per gal (40 g of TNT per 100 ml); the HNO_3 concentration was about 3.5M.

Raffinate: At equilibrium, $\text{Ca}(\text{NO}_3)_2 = 3.75\text{M}$; $\text{HNO}_3 = 0.15\text{M}$; TNT = 0.01M.

4.5 Analyses of Column Solution. The product solution from column 2 is analyzed by a physical method⁵ utilizing specific gravity and refractivity data before precipitating thorium as the oxalate. In this method 10 ml of the solution is placed in a glass cup in a water bath at 25°C , and the refractive index is measured using a Zeiss immersion refractometer. The specific gravity is determined with a hydrometer. With the specific gravity and refractometer values, it is possible, using nomographs, to determine the amounts of thorium and nitric acid present (see Figs. 9 and 10). This rapid method of analysis permits the proper amount of oxalic acid to be determined and added soon after the product has been collected.

More accurate analyses are obtained for the product solution as well as for the raffinate, hexone, and feed solutions by other methods.⁶ These analyses are used for checking production runs and for determining material balances.

4.6 Difficulties Encountered in Column Operation. Early in the experimental runs with the extraction column it was observed that the hexone gradually turned yellow and then green and that there was some heating of the hexone during the operation. During one run, a violent reaction occurred in the hexone tank and in the column itself. The hexone was green at the time and about 5°C above room temperature;

it was about 1M in nitric acid and had shown no test for thorium. In a few moments an autocatalytic reaction took place, which gave off copious fumes of NO_2 and boiled the hexone over the top of the tank.

It is believed that the reaction was between nitric acid and hexone and that the final reaction products were isobutyric acid and acetic acid. The intermediate green product had not been identified at the time of writing. It has been found that the reaction can be minimized by washing the hexone with distilled water after each run. However, since the increase of isobutyric acid in the hexone cuts down the efficiency of the extraction, the hexone is discarded after 20 gal of it has been used to extract thorium from 120 gal of feed solution. Thus, when there is an indication of much thorium in the raffinate as shown by a precipitate with ammonia, the hexone is discarded.

Another difficulty encountered in column operation is the formation of white crystals on the Berl saddles in column 1. This material is insoluble in water or column solutions but partially soluble in acetone. It is apparently an intermediate product in the reaction of hexone and nitric acid. It has been found that this deposit can be removed by a treatment with 3M sodium hydroxide followed by 7M nitric acid.

A dispersed interface in column 1 has also made column operation somewhat difficult. It is due to incomplete separation of the phase, and the dispersed region extends over about 4 ft at the upper end of column 1. In column operation it is possible to keep clear enriched hexone at the top 6 in. of the column, but the dispersed interface which extends 4 ft lower somewhat decreases the effectiveness of the scrubbing section. The dispersed interface is probably due to an impurity in the hexone, feed, or scrubbing solution, but it has not yet been possible to show the cause of the trouble.

5. RARE EARTH SEPARATION IN LARGE COLUMN OPERATION

The thorium nitrate used as the starting material is the mantle grade obtained from the Lindsay Light & Chemical Co. This material when analyzed spectrographically⁷ gave the following results (all these results are based on thorium metal):

Ce	24 ppm	Dy	0.1 ppm	Y	1 ppm
La	8 ppm	Pr	3 ppm	Gd	0.5 ppm
Nd	6 ppm	Sm	0.8 ppm		

After this material had been processed by the extraction column, the following were the maximum limits of rare earths which could be present:

Ce	<0.4 ppm (not detected)
La	<0.04 ppm (doubtful detection)
Nd	<0.2 ppm (not detected)
Pr	<0.1 ppm (not detected)
Sm	<0.2 ppm (not detected)
Y	<0.05 ppm (not detected)
Gd	<0.04 ppm (not detected)
Dy	<0.05 ppm (not detected)

All these figures may be extremely high as they are the minimum amounts possible to detect by the analytical methods used. The actual analysis showed no detectable rare earths present.

Table 1—Materials for 100 Gal of Column Solution

Material	Scrubbing solution, lb	Feed solution, lb
Thorium nitrate tetrahydrate (TNT)		208
Nitric acid	279	279
Calcium nitrate tetrahydrate*	590	590
Water*	331	248
Calcium nitrate tetrahydrate†	57	162
Calcium nitrate solution†	864	676

*Materials used when solutions are made from calcium nitrate tetrahydrate and water

†Materials used when recovered calcium nitrate solution is used. The recovered calcium nitrate solution has a specific gravity of about 1.42.

Table 2—Data Obtained with Extraction Columns

Run	Flow rates gph				Hexone Feed	Acidity of hexone	Th extracted, %	Conc of product soln., g of TNT/100 ml
	Scrub	Feed	Hexone	Water				
1	2.5	5	10.5	3.5	2.1	No HNO ₃	78.1	9.0
2	1	6	10.5	3.25	1.75	0.01N	83.5	21.0
3	1	6	16	3.5	2.66	0.2N	70.5	10.6
4	0.7	6	10.5	2	1.75	0.9	93.4	56.0
5	0.5	5.4	5.4	2	1.0	0.2	68.6	25.2
6	1	7.75	5.4	2	0.7	0.2	31.5	22.4
7	1.5	7.75	16	2.5	2.06	1.8	98.5	53.9
9	1.0	7.5	16	3.8	2.14	1.0	99.3	32.4
10	1.5	6.75	16	3.5	2.38	0.85	98.4	35.0
11	4	7.5	16	3.5	2.14	1.0	90.0	30.0
13	5	4.5	16	3	3.55	1.0	91.0	23.6
14	0	(8)	16	3	2.0	0.6	99.7	58.2
15	0	5	10.5	2.5		0.2	98.9	14.6
17	0.1	7 (?)	16	3	2.28	1.1	99.3	40.1
21	0	7.5	16	3	2.14		94.5	51.9

Table 3—Effects of Variation of Hexone-to-feed Ratio in Column

Run	<u>Hexone</u> Feed	Th extracted, %
4	1.75	93.4
5	1.0	68.6
6	0.7	31.5
9	2.14	99.3
14	2.0	99.7
17	2.28	99.3
13	3.55	91.0

Table 4—Effect of Scrubbing Solution on Extraction

Run	<u>Hexone</u> Feed	Flow rate of scrub, gph	Th extracted, %
11	2.14	4.0	90
7	2.06	1.5	98.5
9	2.14	1.0	99.3
14	2.0	0	99.7

Table 5—Typical Run Data

	Feed tank, gal	Scrubbing tank, gal	Product tank, gal	Raffinate tank, gal
Initial volume	25.0	27.5	26.0	43.0
Final volume	1.0	24.5	15.5	20.0
Net volume	24.0	3.0	10.5	23.0

Fig. 1—Thorium nitrate solvent extraction flowsheet.

Fig. 2—Section of extraction column showing feed inlet tee.

Fig. 3 —Spring suspensions for support of columns.

Fig. 4—Saran helix used in column interface leveler.

Fig. 5—Rotameters and control panel. 1, feed; 2, scrubbing solution; 3, distilled water; 4, hexone; 5, feed control; 6, hexone constant head; 7, scrubbing solution control; 8, feed constant head; 9, distilled water control; 10, scrubbing solution constant head; 11, hexone control.

Fig. 6—Bottom of column showing drains installed.

Fig. 7—Product tanks and stirrers.

Fig. 8—Calcium nitrate recovery system showing storage tanks and filter.

Fig. 9—Nomograph: thorium in product solution.

Fig. 10 — Nomograph: nitric acid in product solution.

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Paper 8.7

EXTRACTION PURIFICATION OF THORIUM NITRATE

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ABSTRACT

The preparation of pure thorium metal entails three main steps: purification of raw materials, preparation of thorium fluoride, and reduction of the fluoride to the metal. This report treats the first step.

The thorium is purified by extraction of its nitrate with hexone from a 3M calcium nitrate, 3M nitric acid solution. The separation from impurities, solvents, salting-out agents, extraction data and curves, reextraction data, etc., are discussed. The physical properties of the solutions involved are tabulated. The groundwork for continuous countercurrent extraction of thorium nitrate with columns is given here, and such extractions are in progress. Column extraction will be treated in detail in later reports. The process appears to be feasible for large-scale application.

1. INTRODUCTION

For preparing pure thorium metal the raw materials (thorium salts) must be purified. For nucleonic purposes the metal and salt must be low in impurities of high capture cross section (boron, cadmium, rare earths, etc.) and have a purity comparable to that of the uranium used in nucleonics.

An extraction technique appeared to be the most promising method of purifying large quantities of thorium to the required degree, analo-

gous to the ether extraction for uranyl nitrate. Taking a lead from the Chicago group's hexone extraction of another tetravalent metal nitrate,² similar operations were performed with thorium nitrate. Various solvents, salting-out agents, and other factors were investigated, and it was found that hexone best suited the need, using calcium nitrate as the salting-out agent. This work is described in Sec. 2.

An outline of the process as now visualized follows:

1. The thorium nitrate (raw material) is dissolved in a nitric acid - calcium nitrate solution, using the proper proportions.
2. This solution is extracted with hexone in a continuous counter-current extractor, thus separating the thorium from most of its impurities (trace amounts of rare earths, Cd, Fe, etc.).
3. The thorium nitrate is reextracted from the hexone with water or dilute nitric acid.
4. Thorium oxalate is precipitated from the water extract.
5. The thorium oxalate is filtered and ignited to thorium dioxide.
6. The thoria is treated with anhydrous hydrogen fluoride, yielding thorium fluoride.
7. The thorium fluoride is reduced and cast to give pure thorium.

The last four steps are discussed in separate reports.³

Any uranium impurity in the thorium nitrate would not be separated by the extraction step. The evidence available⁴ indicates that a separation is made during the precipitation of thorium oxalate; further experiments on this point are in progress. It is also possible that uranium impurities will have to be removed by ether^{1,4} or other solvents prior to the hexone extraction. This, of course, will be necessary only if the uranium impurity proves to be above the tolerance limit.

Simultaneously with the experiments on the solvent extraction of thorium nitrate, a survey of other extraction methods was made. This consisted in complexing the thorium with organic reagents and solvent extraction of the complex. Although a feasible method could probably be developed by this approach, the first few experiments proved less promising than extraction of the thorium nitrate itself.

2. THORIUM NITRATE EXTRACTION

2.1 Thorium Extractions Using Complexing Agents. A number of tetravalent ions form organic solvent-soluble complexes with disalicythylenediimine or its derivatives.⁵ Thus a complex of thorium with di-(2,3-dihydroxy-5 or 6 *tert*-butylbenzal)ethylenediimine was extracted from an acetate-buffered solution with chloroform. The percentage of the thorium extracted by chloroform (aqueous and organic layers of equal volume) varied with the pH as follows:

pH	Th extracted, %
2.5	12.6
3.8	25.0
6.2	61.0

Using disalicylethylenediimine itself as the complexing agent and chloroform, the following percentages of the total thorium were extracted¹⁰ by a single treatment (aqueous and organic layers of equal volume):

pH	Th extracted, %
4.5	1
5.5	8
6.0	5

These results were considered too low, or at least inferior to the hexone extraction of thorium nitrate, and no further similar experiments were tried.

An odd complex of thorium is formed with catechol and pyridine,⁶ which is soluble in quinoline. This solvent was found to extract 99.5 per cent of the thorium from a thorium nitrate solution containing pyridine and catechol¹⁰ (phase volumes equal). A similar test with lanthanum, however, showed 30 per cent extraction; hence little purification from rare earths could be achieved. No further tests were made.

2.2 Extraction of Thorium Nitrate Using Salting-out Agents. In general, the behavior of thorium nitrate toward extraction by organic solvents parallels the case of another nitrate which has already been studied.² Relatively few solvents and salting-out agents were investigated; all those employed were previously mentioned in the Chicago reports.²

The Chicago workers found that the solvent best suited to their purpose was hexone (methyl isobutyl ketone) and the most suitable salt was ammonium nitrate. Experiments using thorium nitrate, ammonium nitrate, and hexone were conducted; the nitric acid strength was 1M. Only the concentration of ammonium nitrate was changed, and the percentage of the thorium extracted was measured. In all extractions the volume of the organic phase was equal to the volume of the aqueous phase at the beginning, and the two liquids were shaken vigorously in a separatory funnel for 10 to 15 min. Unless otherwise indicated, the solvents were all saturated with water before use; if

this is not done, sometimes enough water is drawn from the aqueous phase to cause crystallization of the syrupy highly concentrated salt solution. The results of this first series of extractions are given in Table 1.

The data of Table 1 demonstrate the dependency of the percentage of thorium extracted on the salt concentration. Next, the ammonium nitrate strength was dropped, and the nitric acid strength was raised enough to maintain the total nitrate-ion concentration constant. The percentage extracted dropped with the salt concentration, as shown in Table 2.

In order to compare several solvents, they were tested using 10M ammonium nitrate and 1M nitric acid. The results are shown in Table 3.

Nitrates other than ammonium nitrate were tested as salting-out agents. The results are summarized in Table 4.

Using cupric nitrate, the color of the organic phase disclosed the presence of considerable copper. In the case of manganous nitrate, the thorium obtained in the analysis of the organic phase was brown, indicating that some manganese was extracted. Silver nitrate was considered too expensive, and of the remaining two salts the calcium nitrate is superior to aluminum nitrate in salting-out action, is more soluble, and is much cheaper. The calcium nitrate was found to offer some advantages over ammonium nitrate and was chosen for the remainder of the work. Some extraction of calcium nitrate does occur; this is discussed in Sec. 2.5.

Some of the solvents listed in Table 3 appeared promising, namely, hexone, nitromethane, acetophenone, cyclohexanone, diethyl cellosolve, and butyl phosphate. The last was eliminated because of its probable slow decomposition. Acetophenone was eliminated because of its high density (1.03). Hexone and cyclohexanone were chosen for further study primarily because they were readily available and did extract practical quantities of thorium nitrate. By no means have the other solvents been eliminated; some may be far superior to hexone and cyclohexanone. These, as well as new solvents, will be investigated and reported at a later date.

Cyclohexanone would appear to be superior to hexone because of its greater power to extract thorium nitrate, but this factor did not compensate for its disadvantages. The reasons for concentrating work on hexone rather than cyclohexanone were:

1. Hexone gave a much better separation from the rare earths (see Sec. 2.3).

2. The density of hexone (0.80) is much more favorable than the density of cyclohexanone (0.95). Thus when thorium nitrate is ex-

tracted by the organic phase the density in the case of cyclohexanone becomes greater than unity which would complicate the operation of the water-filled column in which the thorium nitrate is reextracted.

3. Cyclohexanone is much more soluble in water than is hexone.

4. Cyclohexanone has sometimes given a precipitate when allowed to stand in contact with solutions containing nitric acid. The precipitate may be adipic acid.

In case a solvent whose density is greater than 1 (e.g., nitromethane, $d = 1.13$) is finally chosen, then in column operation it will be necessary to feed the thorium-rich solvent into the top of the water-reextraction column rather than the bottom, but this should cause little difficulty.

In Fig. 1 are given some extraction curves for cyclohexanone and 50 per cent cyclohexanone, 50 per cent hexone mixtures. The high extractions of cyclohexanone are shown, and it is of interest that this curve has a negative slope. It should be pointed out that the curve for the mixed solvents, hexone and cyclohexanone (all using 3M calcium nitrate), lies about halfway between the two separate curves for each solvent alone. At one time consideration was given to using this 50-50 mixture, combining the high extractability of cyclohexanone with the low density of hexone, but the faults of cyclohexanone prevented this.

Additional extraction data were obtained using hexone and calcium nitrate. They are shown in Table 5.

The extraction data using 3M calcium nitrate (Table 5) are graphed in Fig. 2. Plotting the percentage of thorium nitrate extracted against thorium nitrate concentration gives separate curves for each nitric acid concentration. For the lower concentrations of thorium nitrate, the percentage of thorium extracted decreases with decreasing nitric acid concentration, but at 3M nitric acid the curve has a zero or perhaps slightly negative slope. This characteristic should enhance the extraction of thorium nitrate in a continuous countercurrent column. Thus essentially all the thorium may be removed if the nitric acid strength is maintained above 1M.

Figure 3 illustrates the removal of thorium nitrate by four successive extractions with each volume of hexone equal to the volume of the aqueous phase. Initially the solution contained 50 g of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ per 100 ml of solution and was 3M in calcium nitrate and 3M in nitric acid. The four extractions removed 92.5 per cent of the total thorium. The third and fourth extractions removed smaller percentages of the remaining thorium, presumably because of the lowering of the nitric acid strength.

2.3 Separation of Elements of High Capture Cross Section by Solvent Extraction. The distribution of elements of high capture cross section (rare earths, cadmium, and boron) between organic solvents and water-salt solutions has been studied. Chicago workers² have reported previously the distribution (separation factors) for various elements, including boron and lanthanum, between various organic solvents and 10M NH_4NO_3 , 1M HNO_3 . Since the main concern lies with the distribution of elements of high capture cross section between organic solvents and water solutions containing the salting-out agent as well as thorium nitrate, this has been of interest but not of direct application.

(a) Distribution between 10M Ammonium Nitrate, 1M Nitric Acid Solution, and Organic Solvents. The distribution coefficient for the element noted, the percentage extracted (for equal volumes of organic solvent and water solutions) into the organic phase, and the concentration of the element in milligrams per milliliter for the system 10M NH_4NO_3 , 1M HNO_3 and organic solvent were determined and are given in Table 6.

The distribution coefficient for cerium was found to be the same whether it was initially in the trivalent or tetravalent state. In the latter state it was rapidly reduced to the cerous state by the solvent.

The distribution coefficient for rare earths (Table 6) refers to the distribution of rare earth activity (mostly 300-day cerium in equilibrium with its 17.5-min praseodymium daughter) between a solution containing initially 0.215M $\text{Th}(\text{NO}_3)_4$, 10M NH_4NO_3 , 1M HNO_3 , and cyclohexanone. The presence of thorium nitrate seems to raise the distribution coefficient. The behavior of boron is discussed in Sec. 2.7.

(b) Distribution of Tracer Rare Earths between Thorium Nitrate - Calcium Nitrate - Nitric Acid Solutions and Organic Solvents. The distribution of tracer rare earths (described above) between thorium nitrate - calcium nitrate - nitric acid solutions and organic solvents has been studied. The results show very definitely that the presence of thorium nitrate increases the extraction of rare earths by the organic phase. This is to be expected in view of the fact that salting-out increases with increasing ionic charge.

A calcium nitrate solution (3M, 1.08 ml), containing varying amounts of thorium nitrate and nitric acid, and 3000 div/min of rare earth activity (corresponding roughly to 2.1×10^7 dis/min) were shaken with 1 ml of organic solvent for 5 min. A 0.13-ml aliquot of the organic phase was then removed, and the rare earth activity was isolated by the following scheme:

The activity in the lanthanum fluoride thus obtained was counted by reading on the electroscope. This method yielded blanks (activity due to thorium disintegration series) of less than 0.35 div/min for concentrations of thorium nitrate as high as 0.9M. The data are given in Table 7. The purification factor is defined as the ratio of the percentage of thorium extracted to the percentage of rare earths extracted when equal volumes of organic solvent and aqueous solution are used, but in the table the ratio of the volumes is 1 to 1.08. The data for the percentage of thorium extracted were taken directly from the curves of Fig. 1 and Fig. 2. Where the thorium molarity was zero, the percentage extracted was obtained by extrapolating the curves to zero.

It is to be noted that the purification factors for cyclohexanone are poor as compared to those of hexone. The purification factor for hexone decreases rapidly with increasing thorium concentration.

2.4 Reextraction of Thorium Nitrate. The removal of the thorium nitrate from its organic solvent is accomplished by extraction with water or sometimes with dilute nitric acid. For the most part these separations have been quite efficient, above 95 per cent of the thorium nitrate in a hexone solution being extracted by an equal volume of water. The removal is slightly poorer in the case of cyclohexanone, and 1.5M HNO₃ is slightly inferior to water, as shown by the results in Table 8. The organic solutions used contained small quantities of nitric acid and calcium nitrate.

2.5 Distribution of Nitric Acid and Calcium Nitrate. As Fig. 2 shows, the nitric acid concentration is important, and its behavior when extracted with hexone was studied. In aqueous thorium nitrate

solutions, distinction can be drawn between nitric acid formed by hydrolysis and nitric acid present in excess of this amount. This excess nitric acid is called "added" nitric acid, and it is this fraction whose extraction behavior is important.

Solutions from various extraction stages were analyzed for added nitric acid by adding an excess of standard ammonium hydroxide, filtering and washing, and back-titrating the excess base with standard acid, using methyl red indicator. The thorium hydroxide formed was ignited to thoria and weighed, and from these data the added nitric acid was calculated.

Two series of solutions were extracted with hexone (aqueous and organic layers of equal volume), and the organic layer was analyzed for added nitric acid. When the percentages of nitric acid were calculated, the volume changes on extraction were taken into consideration (see Sec. 2.6). The first series of solutions was 3M in calcium nitrate and 3M in added nitric acid; the second was 3M in calcium nitrate and 2M in added nitric acid. The thorium nitrate concentrations varied in each series. Results are shown in Table 9.

The data in this table show that the hexone extracts nitric acid more efficiently than it does the thorium nitrate, a fact which deserves serious consideration in the operation of an extraction column.

An experiment was made to determine what fraction of nitric acid in hexone was reextracted when treated with water. Four solutions, each 3M in calcium nitrate and nitric acid and with varying concentrations of thorium, were extracted with hexone (single treatment with equal volumes), and the hexone layers were reextracted with water (single treatment with equal volumes). The hexone, depleted of its thorium, was then titrated with standard alkali. The data are given in Table 10. The volume changes (Sec. 2.6) were taken into account.

Tables 9 and 10 show that, from the acidified calcium nitrate solutions, nitric acid is readily extracted by hexone and that reextraction of the hexone with water does not remove all the acid (with a single treatment using equal volumes). Thus thorium nitrate enters the hexone fairly easily and is reextracted by water nearly quantitatively, while the nitric acid enters the hexone very readily and is only reextracted by water with some difficulty.

A small portion of calcium nitrate was shown to enter the hexone phase. Rough analyses for calcium were made on the hexone layers from extractions of the standard 3M $\text{Ca}(\text{NO}_3)_2$, 3M HNO_3 solutions, giving the results shown in Table 11. This small amount of calcium should cause no trouble since most will be separated in the subsequent thorium oxalate precipitation. Further, considerable calcium salts can be tolerated in the metal reduction without appreciable effect on the yields or quality.

2.6 Physical Properties of Solutions. In order to design and operate a countercurrent extraction column, it is helpful to have such physical properties of the solutions involved as densities, viscosities, crystallization temperatures, and volume changes on extraction. These have been measured for a number of solutions and are given in Tables 12 through 16 for the acid and salt concentrations stated.

2.7 Miscellaneous. (a) Behavior of Boron. A cursory investigation was made into the contamination of thorium nitrate solutions with boron from pyrex. While the degree of contamination must vary with time of contact, surface relationships, nature of solution, and other factors, a rough result was obtained by analyzing a solution from extraction work where pyrex ware had been used. The analytical method was spectrographic.⁷ Based on thorium, the solutions picked up boron corresponding to approximately 0.6 ppm.

It was believed that any boron picked up in these stages would be eliminated at later stages, namely, during the precipitation of thorium oxalate and the preparation of thorium fluoride, where boron would be volatilized away as its trifluoride. This hypothesis was checked¹¹ by adding a known quantity of boric acid to a thorium nitrate solution (1000 ppm boron, based on thorium) and precipitating thorium oxalate (see Paper 8.1). Analysis of the oxalate showed 1.6 ppm of boron. This was converted to thorium fluoride, the analysis of which showed less than 0.1 ppm of boron. It thus appears that the use of pyrex glass is permissible.

(b) Spontaneous Reaction of Thorium Nitrate-Hexone Solutions. On two occasions, solutions of thorium nitrate in hexone from extraction work began to boil spontaneously with foaming and the liberation of a substance smelling of isobutyric acid. One solution had been standing about 5 hr and the other about 36 hr before the reaction started. Each solution was about half a liter in quantity. The concentration of thorium nitrate in neither solution was known, but it was high in each. Evidently the nitrates $[\text{Th}(\text{NO}_3)_4$ and $\text{HNO}_3]$ caused chemical oxidation of the ketone.

More information was obtained by extracting a thorium nitrate solution (3M in calcium nitrate, 3M in nitric acid, and 25 g $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ per 100 ml). This was divided into three parts. One part was heated; at 95°C it turned yellow, and at 105°C it reacted suddenly and boiled up, giving off isobutyric acid. A second portion was allowed to stand at room temperature and after a day had turned yellow and smelled of isobutyric acid but did not boil. The third was kept at 0 to 10°C where it underwent no noticeable change in 5 days.

The reaction should cause little harm if the extracts are not permitted to stand but treated with water at once.

(c) Mesothorium. Mesothorium is not expected to be extracted by the hexone treatment and thus will appear in the raffinate from any column work. It may prove to be profitable to recover this material, which could probably be done by adding either barium or lead nitrate and then precipitating the sulfate.

(d) Behavior of Uranium. It would be expected that uranyl nitrate is readily extractable by hexone, and such is the case. The solvent is said¹² to be comparable with ether. Tests showed that using a volume of hexone equal to that of the aqueous solution (10M NH_4NO_3 , 1M HNO_3) about 90 per cent of the uranium is extracted. Thus uranium is extracted even more easily than thorium.

3. CONCLUSIONS

A process has been developed by which thorium nitrate can be purified to a high degree. Thorium nitrate is extracted into an organic solvent from an aqueous solution and then reextracted by water. This procedure was adopted from a process used for another metal by the Chicago group and parallels the ether extraction purification of uranyl nitrate. At present the process appears to be feasible for large-scale application. Though satisfactory at its present stage of development, additional modifications, such as new solvents, may offer still more advantages, and work on improvements will continue.

Table 1—Extraction of $\text{Th}(\text{NO}_3)_4$ by Hexone
from NH_4NO_3 – HNO_3 Solutions

Concentration of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, g per 100 ml of solution	Molarity		Th extracted, %
	HNO_3	NH_4NO_3	
25	1	0	0.15
25	1	2	1.01
25	1	4	2.81
25	1	6	6.78
25	1	8	13.7
25	1	10	19.8

Table 2—Extraction of $\text{Th}(\text{NO}_3)_4$ by Hexone from NH_4NO_3 – HNO_3 Solutions

Concentration of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, g per 100 ml of solution	Molarity		Th extracted, %
	HNO_3	NH_4NO_3	
25	1	10	20
25	3	8	16
25	5	6	14

Table 3—Extraction of $\text{Th}(\text{NO}_3)_4$ by Various Solvents from 10M NH_4NO_3 and 1M HNO_3

Solvent	Concentration of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, g per 100 ml of solution	Th extracted, %
Hexone	5.4	21
Nitromethane	5.4	11
α -Naphthyl methyl ether	5.1	0.35
Diethyl oxalate	5.2	5.4
Acetophenone	5.9	37
Cyclohexanone	25	85
Diethyl cellosolve	25	70
Butyl phosphate	25	91

Table 4—Extraction of $\text{Th}(\text{NO}_3)_4$ from Various Salt Solutions

Salt	Molarity		Solvent	Concentration of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, g per 100 ml of solution	Th extracted, %
	Salt	HNO_3			
$\text{Cu}(\text{NO}_3)_2$	3.8	0.5	Cyclohexanone	9	~100
$\text{Mn}(\text{NO}_3)_2$	4.2	1.4	Cyclohexanone	25	~100
AgNO_3	7	1.1	Cyclohexanone	20	58
$\text{Al}(\text{NO}_3)_3$	1.7	0.9	Hexone	8	36
$\text{Al}(\text{NO}_3)_3$	1.7	0.9	Cyclohexanone	8	95
$\text{Al}(\text{NO}_3)_3$	1.9	0.5	Hexone	8	49
$\text{Al}(\text{NO}_3)_3$	1.9	0.5	Cyclohexanone	8	~100
$\text{Ca}(\text{NO}_3)_2$	5	0.7	Hexone	12.5	90
$\text{Ca}(\text{NO}_3)_2$	3	0	Hexone	30	35
$\text{Ca}(\text{NO}_3)_2$	3	0	Hexone	50	50
$\text{Ca}(\text{NO}_3)_2$	5	0.7	Cyclohexanone	12.5	~100
$\text{Ca}(\text{NO}_3)_2$	5	0	Cyclohexanone	10	96
$\text{Ca}(\text{NO}_3)_2$	3	0	Cyclohexanone	10	92

Table 5—Extraction of $\text{Th}(\text{NO}_3)_4$ with Hexone from HNO_3 — $\text{Ca}(\text{NO}_3)_2$ Solutions of Various Concentrations

Molarity		Concentration of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, g per 100 ml of solution	Th extracted, %
$\text{Ca}(\text{NO}_3)_2$	HNO_3		
2.1	0	86	43
3	0	10	11
3	0	30	35
3	0	50	50
5	0	10	91
2	5	10	50
2	5	30	41
2	5	50	44
3	1	10	34
3	1	30	45
3	1	50	56
3	2	10	49
3	2	15	49
3	2	25	50
3	2	35	52
3	2	45	56
3	2	50	63
3	3	10	60
3	3	15	57
3	3	25	56
3	3	30	57
3	3	35	59
3	3	45	59
3	3	50	53
5	0.7	12	90

Table 6—Extraction of Elements from 10M NH_4NO_3 , 1M HNO_3 by Organic Solvents

Solvent	Element	Conc. of element, mg/ml	% extracted by organic phase	$K = \frac{\text{Conc. in org. phase}}{\text{Conc. in H}_2\text{O phase}}$
Hexone	La	4.3	0.1	1×10^{-3}
Hexone	Cd	21.6	<0.2	$<2 \times 10^{-3}$
Hexone	B	0.09	0.25	2.5×10^{-3}
Cyclohexanone	La	15.1	0.47	5.1×10^{-3}
Cyclohexanone	Ce	13.4	2.3	25×10^{-3}
Cyclohexanone	Cd	9.2	0.44	4.8×10^{-3}
Cyclohexanone	Rare earth*	(Trace quantities)	4.88	56×10^{-3}

* H_2O solution initially was 0.215M $\text{Th}(\text{NO}_3)_4$, 10M NH_4NO_3 , 1M HNO_3 .

Table 7—Extraction of Tracer Rare Earths from 3M $\text{Ca}(\text{NO}_3)_2$ - HNO_3 - $\text{Th}(\text{NO}_3)_4$ Solutions by Organic Solvents

Solvent	Molarity		Th extracted, %	Rare earths extracted, %	Approx. purification factor
	$\text{Th}(\text{NO}_3)_4$	HNO_3			
Cyclohexanone	0.00	0	92	4.5	23
Cyclohexanone	0.215	0	92	7.0	13
Cyclohexanone	0.430	0	91	5.4	13
Hexone	0.215	0	54	0.11	490
Hexone	0.00	1	28	0.03	930
Hexone	0.215	1	35	0.10	350
Hexone	0.430	1	42	0.31	140
Hexone	0.860	1	56	1.1	51
Hexone	0.00	3	57	0.14	410
Hexone	0.215	3	56	0.14	400
Hexone	0.860	3	54	0.47	115

Table 8—Reextraction of $\text{Th}(\text{NO}_3)_4$ from Organic Solvents by Water and by Dilute Nitric Acid

Solvent	Approx. conc. of thorium, g of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ per 100 ml of organic solution	Th extracted by water, %	Th extracted by 1.5M HNO_3 , %
Hexone	0.6	96.5	
Hexone	2.5	98.0	
Hexone	10	96.6	96.2
Hexone	25	99.1	99.3
Cyclohexanone	9	99.0	82.7
Cyclohexanone	15	91.0	80.0
Cyclohexanone	43	93.6	78.0

Table 9—Extraction of Added Nitric Acid by Hexone
from $\text{Ca}(\text{NO}_3)_2$ - HNO_3 - $\text{Th}(\text{NO}_3)_4$ Solutions

	$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ per 100 ml of solution, g			
	15	25	35	45
Series 1. 3M $\text{Ca}(\text{NO}_3)_2$, 3M HNO_3				
Molarity of HNO_3 in hexone	1.92	1.93	1.80	1.86
HNO_3 extracted by hexone, %	73	75	72	76
Series 2. 3M $\text{Ca}(\text{NO}_3)_2$, 2M HNO_3				
Molarity of HNO_3 in hexone	1.40	1.38	1.38	1.32
HNO_3 extracted by hexone, %	77	77	79	78

Table 10—Reextraction of Nitric Acid from Hexone by Water

	$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ per 100 ml of solution, g		
	5	25	50
Molarity of HNO_3 in hexone after first extraction (data in Table 9)	1.9	1.9	1.85
Molarity of HNO_3 in hexone after reextraction with water	0.29	0.62	0.72
HNO_3 removed, %	88	74	69

Table 11—Calcium Nitrate Extraction by Hexone

Concentration of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, g per 100 ml of solution	Molarity		Approx. per cent of total $\text{Ca}(\text{NO}_3)_2$ extracted by hexone	Approx. wt. ratio (Th extr./Ca extr.)
	$\text{Ca}(\text{NO}_3)_2$	HNO_3		
10	3	3	<0.1	<190
25	3	3	0.2	240
30	3	3	0.7	80
50	3	3	0.9	100

Table 12—Properties of Aqueous and Hexone Solutions*

	Th(NO ₃) ₄ ·4H ₂ O per 100 ml of solution, g				
	0	15	25	35	45
Original solution [3M in Ca(NO ₃) ₂ , 3M in HNO ₃]					
Density at 25°, g/ml	1.434	1.528	1.592	1.655	1.715
Viscosity at 25°, centipoises	4.57	6.89	9.20	12.63	17.64
Hexone solution (from extraction of 50 ml of original solution with 50 ml of hexone)					
Volume of hexone layer, ml	55.1	57.0	58.1	59.9	61.1
Volume of aqueous layer, ml	44.9	43.0	41.9	40.1	38.9
Density of hexone layer at 25°, g/ml	0.873	0.9306	0.9661	1.007	1.047
Viscosity of hexone layer at 25°, centipoises	1.025	1.445	1.740	2.202	2.790
Th(NO ₃) ₄ ·4H ₂ O per 100 ml of solution, g		7.5	12.0	17.3	21.9
Thorium extracted, %		57	56	59	59
Aqueous solution (from reextraction of 25 ml of above hexone solution with 25 ml of water)					
Volume of hexone layer, ml		20.4	20.3	20.2	20.0
Volume of aqueous layer, ml		29.6	29.7	29.8	30.0
Density of aqueous layer at 25°, g/ml		1.086	1.114	1.145	1.175
Viscosity of aqueous layer at 25°, centipoises		1.092	1.163	1.256	1.334

*The material in this table is given graphically as follows: Densities of original, hexone, and water-reextraction solutions for varying strengths of thorium nitrate, Fig. 4. Densities of aqueous calcium nitrate-nitric acid-thorium nitrate solutions and hexone-thorium nitrate solutions, Fig. 5. Viscosities of thorium nitrate-nitric acid-hexone solutions, Fig. 6. Viscosities of original thorium nitrate-nitric acid-water solutions, Fig. 7. Viscosities of thorium nitrate-nitric acid-water solutions and hexone solutions from extraction, Fig. 8.

Table 13 — Properties of Aqueous and Hexone Solutions*

	Th(NO ₃) ₄ ·4H ₂ O per 100 ml of solution, g				
	0	15	25	35	45
Original solution [3M in Ca(NO ₃) ₂ , 2M in HNO ₃]					
Density at 25°, g/ml	1.406	1.506	1.566	1.631	1.693
Viscosity at 25°, centipoises	3.89	6.17	7.98	10.88	15.19
Hexone solution (from extraction of 50 ml of original solution with 50 ml of hexone)					
Volume of hexone layer, ml	53.0	54.8	56.0	57.5	59.0
Volume of aqueous layer, ml	47.0	45.2	44.0	42.5	41.0
Density of hexone layer at 25°, g/ml	0.8519	0.9056	0.9407	0.9803	1.023
Viscosity of hexone layer at 25°, centipoises	0.882	1.227	1.525	1.946	2.545
Th(NO ₃) ₄ ·4H ₂ O per 100 ml of solution, g		6.7	11.1	15.9	21.2
Thorium extracted, %		49	50	52	56
Aqueous solution (from reextraction of 25 ml above hexone solution with 25 ml water)					
Volume of hexone layer, ml		21.6	21.0	20.8	20.5
Volume of aqueous layer, ml		28.4	29.0	29.2	29.5
Density of aqueous layer at 25°, g/ml		1.070	1.098	1.131	1.164
Viscosity of aqueous layer at 25°, centipoises		1.065	1.116	1.213	1.309

*The material in this table is given graphically as follows: Densities of original, hexone, and water-reextraction solutions for varying strengths of thorium nitrate, Fig. 4. Densities of aqueous calcium nitrate-nitric acid-thorium nitrate solutions and hexone-thorium nitrate solutions, Fig. 5. Viscosities of thorium nitrate-nitric acid-hexone solutions, Fig. 6. Viscosities of original thorium nitrate-nitric acid-water solutions, Fig. 7. Viscosities of thorium nitrate-nitric acid-water solutions and hexone solutions from extraction, Fig. 8.

Table 14—Crystallization Temperatures for
3M $\text{Ca}(\text{NO}_3)_2$, 3M HNO_3 Solutions

Th(NO_3) ₄ 4H ₂ O per 100 ml of solution, g	Crystallization temperature, °C
1	<2
5	<3
25	10–11
50	23–24

Table 15—Properties of Hexone

Density at 25°C of hexone saturated with water, g/ml	0.8009
Viscosity at 25°C of hexone saturated with water, centipoises	0.5925
Boiling point (760 mm Hg), °C	118
Freezing point, °C	–85
Solubility in water, %	2.0 (reference 8)
Water solubility in hexone, %	2.2 (reference 8)

Table 16—Extraction of Nitric Acid from Water by Hexone*⁹

Molarity HNO_3		Density (at 25°C) of hexone solution, g/ml
In original water layer	In hexone after extraction	
15.6	7.01	1.057
12.5	5.16	0.992
9.36	3.56	0.941
6.24	2.15	0.890
3.12	0.797	0.834
1.56	0.257	0.811
0.624	0.041	0.801

*Nothorium nitrate was used. Aqueous and organic phases
of equal volume at beginning, dry hexone was used.

Fig. 1—Extraction of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ into various solvents. Varying concentrations of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.

Fig. 2—Extraction of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ into hexone from $3\text{M Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Varying HNO_3 solutions.

Fig. 3—Successive extractions of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ into hexone from 3M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 3M HNO_3 solution.

Fig. 4—Density of solutions from extraction of $\text{Th}(\text{NO}_3)_4$ with hexone. $\circ$, original solution, 1M HNO_3 , 3M $\text{Ca}(\text{NO}_3)_2$. $\square$, original solution, 2M HNO_3 , 3M $\text{Ca}(\text{NO}_3)_2$. $\triangle$, original solution, 3M HNO_3 , 3M $\text{Ca}(\text{NO}_3)_2$. $\bullet$, methyl isobutyl ketone solution from the extraction of 50 ml of original 2M HNO_3 solution with 50 ml of ketone. $\circ$, methyl isobutyl ketone solution from the extraction of 50 ml of original 3M HNO_3 solution with 50 ml of ketone. $\diamond$, water solution from the extraction of 25 ml of ketone solution ($\bullet$) with 25 ml of H_2O . ∇ , water solution from the extraction of 25 ml of ketone solution ($\circ$) with 25 ml of H_2O .

Fig. 5—Density of ketone and H₂O solutions of Th(NO₃)₄, Ca(NO₃)₂, and HNO₃. □, original solution, 2M HNO₃, 3M Ca(NO₃)₂. Δ, original solution, 3M HNO₃, 3M Ca(NO₃)₂. ●, methyl isobutyl ketone solution from the extraction of 50 ml of original 2M HNO₃ solution with 50 ml of ketone; analysis showed HNO₃ concentration from 1.32M to 1.405M. ○, methyl isobutyl ketone solution from the extraction of 50 ml of original 3M HNO₃ solution with 50 ml of ketone, analysis showed HNO₃ concentration ranging from 1.795M to 1.935M.

Fig. 6—Viscosity of ketone solutions of Th(NO₃)₄ and HNO₃. ●, methyl isobutyl ketone solution from the extraction of 50 ml of original 2M HNO₃ solution (Fig. 5) with 50 ml of ketone; analysis showed HNO₃ concentration ranging from 1.32M to 1.405M. ○, methyl isobutyl ketone solution from the extraction of 50 ml of original 3M HNO₃ solution (Fig. 5) with 50 ml of ketone, analysis showed HNO₃ concentration ranging from 1.795M to 1.935M.

Fig. 7—Viscosity of solutions from extraction of $\text{Th}(\text{NO}_3)_4$ with hexone. $\circ$, original solution, 1M HNO_3 , 3M $\text{Ca}(\text{NO}_3)_2$. $\square$, original solution, 2M HNO_3 , 3M $\text{Ca}(\text{NO}_3)_2$. $\triangle$, original solution, 3M HNO_3 , 3M $\text{Ca}(\text{NO}_3)_2$.

Fig. 8—Viscosity of solutions from extraction of $\text{Th}(\text{NO}_3)_4$ with hexone. $\bullet$, methyl isobutyl ketone solution from the extraction of 50 ml of original 2M HNO_3 solution (Fig. 7) with 50 ml of ketone. $\circ$, methyl isobutyl ketone solution from the extraction of 50 ml of original 3M HNO_3 solution (Fig. 7) with 50 ml of ketone. $\diamond$, water solution from the extraction of 25 ml of ketone solution ($\bullet$) with 25 ml of H_2O . ∇ , water solution from the extraction of 25 ml of ketone solution ($\circ$) with 25 ml of H_2O .

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Paper 9.1

THERMAL-NEUTRON FISSION CROSS SECTION OF Th^{229}

By Martin H. Studier, Albert Ghiorso, and French Hagemann

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ABSTRACT

The fission cross section of Th^{229} for thermal neutrons has been determined to be $45 \times 10^{-24} \text{ cm}^2$ within 25 per cent.

1. INTRODUCTION

The probability of neutron-induced fission is greater for isotopes which contain an odd number of neutrons than for those which have an even number, according to the Bohr-Wheeler theory. Notable examples are Pu^{239} , U^{235} , and U^{233} , each of which has a very large fission cross section for thermal neutrons. Another isotope of the odd-number-neutron type of nucleus is Th^{229} , an alpha emitter having a half life of about 7000 years, which is produced¹ by alpha decay of U^{233} . It has been found that Th^{229} also undergoes fission with thermal neutrons with a moderately large cross section.

The fission measurements have necessarily been limited to sub-microgram samples of Th^{229} since only milligram quantities of U^{233} have as yet become available; however, development of sensitive fission counters and the availability of the large neutron flux produced by the chain-reacting pile have made such measurements feasible.

2. CHEMICAL SEPARATION

The samples used for these measurements were obtained by allowing a solution of U^{233} in 0.1M nitric acid to decay for a suitable length of time and then separating and purifying the Th^{229} which had been

formed. The thorium was separated from the uranium solution by coprecipitation with zirconium iodate; the conditions of precipitation were about 0.2 mg of zirconium per milliliter of solution and a final iodate concentration of 0.05M. Further purification was achieved by separating the zirconium iodate by centrifugation, dissolving in sulfur dioxide-water, and reprecipitating as before. A blank run with U^{233} tracer showed that four or five such cycles served to decontaminate completely from uranium.

Sample 1 was purified by six iodate cycles. In order to reduce the amount of carrier to obtain a film sufficiently thin for fission counting, the Th^{229} was finally coprecipitated with 0.1 mg of lanthanum fluoride and mounted on platinum.

Sample 2 was put through three iodate cycles; then the thorium was coprecipitated with lanthanum fluoride (1 mg per milliliter of solution) after oxidizing with silver ion-persulfate. The lanthanum fluoride was metathesized to hydroxide with sodium hydroxide solution and dissolved in 0.1M nitric acid. The oxidizing cycle was repeated, and the Th^{229} was finally coprecipitated with 0.1 mg of zirconium iodate and mounted on platinum. The purpose of fluoride precipitations from oxidized solution was to ensure that any accidental contamination by Pu^{239} would be removed as well as to separate further from U^{233} .

Sample 3 was prepared from sample 2 after fission measurements had been carried out. The sample was dissolved from the platinum plate with nitric-hydrofluoric acid mixture, put through an oxidizing cycle, and remounted as before, using 0.1 mg zirconium as a carrier.

Sample 4 was prepared from samples 1 and 3. The material was carried through additional oxidizing and iodate cycles and coprecipitated with lanthanum fluoride. The fluoride was converted to hydroxide and dissolved in 0.05M nitric acid, and the Th^{229} was extracted with 0.15M thenoyl trifluoroacetone (TTA)² in benzene. The benzene phase was reextracted with 10M nitric acid, and the nitric acid solution was evaporated on platinum, thus giving an essentially carrier-free sample.

3. FISSION MEASUREMENTS

The fission measurements were carried out in the thermal column of the Argonne CP-3 heavy-water pile. The fission-counting apparatus is described elsewhere.³ Comparison was made of the fission-counting rates of the Th^{229} samples with the fission-counting rates of standard samples of U^{233} or Pu^{239} measured under conditions of identical neutron flux.

Fission cross sections for Th^{229} were calculated from the relation

$$\sigma_{\text{fiss}}(\text{Th}^{229}) = \frac{f(\text{Th}^{229})}{f(\text{std.})} \times \frac{\text{wt.}(\text{std.})}{\text{wt.}(\text{Th}^{229})} \times \frac{229}{A(\text{std.})} \times \sigma_{\text{fiss}}(\text{std.})$$

where $f(\text{Th}^{229})$ and $f(\text{std.})$ = observed fission-counting rates of sample and standard, respectively, and $A(\text{std.})$ = mass number of the standard. The values $521 \times 10^{-24} \text{ cm}^2$ (reference 4) for U^{233} and $765 \times 10^{-24} \text{ cm}^2$ (reference 5) for Pu^{239} were used for the fission cross sections of the standards for the neutrons in the thermal column of the Argonne CP-3 pile. The weights of the standards were calculated from the alpha counts using 1.62×10^5 years for the half life⁶ of U^{233} and 2.41×10^4 years (reference 7) for Pu^{239} . The sample weights were also determined by alpha counting, using 7000 years for the Th^{229} half life. Since the U^{233} parent of the Th^{229} contained some U^{232} impurity,¹ appreciable amounts of RdTh impurity produced by alpha decay of the U^{232} were present in the samples. A correction for this impurity was made by determining the $\text{Th}^{229}/\text{RdTh}$ ratio by means of the pulse analyzer.⁸ Since the fission cross section of RdTh has been determined to be negligible,⁹ no correction of the fission-counting rate was necessary. The results of the measurements are summarized in Table 1.

Examination of the data indicates that Th^{229} has an appreciable fission cross section for slow neutrons. It is evident that this fission is actually due to Th^{229} and not to contamination by uranium or plutonium isotopes since further purification of samples 1, 2, and 3 did not result in a decrease in the calculated fission cross section, even though the purification would have reduced such impurities by more than a hundredfold.

The discrepancy between the cross sections observed for samples 1, 2, and 3 and for sample 4 can probably best be explained by differences in sample thicknesses since the first three samples were each mounted with about 0.1 mg of carrier, whereas the fourth sample was carrier-free. Self-absorption of the fission fragments may have reduced the observed fission-counting rates of the first three samples, thus giving an apparently lower value for the cross section.

These measurements were carried out during the period of improvement of the fission counters. The last measurement on sample 4 is considered to be more reliable since it was made using one of the later fission-chamber designs in which the sensitivity had been greatly increased as is evident by comparison of the fission-counting rate to the background.

The most probable value of the cross section from these considerations is $45 \times 10^{-24} \text{ cm}^2$, and the possible error is judged to be about 25 per cent.

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Table 1 — Determination of Fission Cross Section of Th^{229}

Sample	Alpha activity, c/min		Wt. of Th^{229} , 10^{-8} g	Fission, c/min		Alpha activity, c/min	Standards			$\sigma_{\text{fiss}}(\text{Th}^{229})$, 10^{-24} cm ²
	(Th^{229} + RdTh)	Th^{229}		Background	Net		Wt. of U^{233} , 10^{-8} g	Wt. of Pu^{239} , 10^{-8} g	Fission, c/min	
1	4,010	2,740	1.06	1.5	0.9	9500	86.84		1,060	36
2	27,500	18,800	7.30	2.1	9.0	9500	86.84		2,118	26
3	20,200	13,900	5.36	3.0	9.0	9500	86.84		3,040	25
4	5,590	3,820	1.48	188	85	235	2.15		1,440	44
4	5,590	3,820	1.48	510	417	235	2.15		6,700	46
4	5,590	3,820	1.48	50	8300	235	2.15		138,000	45
						645		0.90	84,000	44

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Paper 9.2

A NEW RADIOACTIVE SERIES: THE PROTACTINIUM SERIES

By Martin H. Studier and Earl K. Hyde

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ABSTRACT

A new series of radioactive isotopes has been produced by deuteron and helium-ion bombardments of thorium. The isotopes in the new series are shown to be the following:

1. INTRODUCTION

Three radioactive series, the thorium series, the uranium-radium series, and the actinium series, are known to occur in nature. These series are often called the $(4n)$, the $(4n+2)$, and the $(4n+3)$ series, respectively, after the general formula for the mass numbers of the isotopes in each of the three series. For a long time a fourth series, the $(4n+1)$, was predicted and sought for, but it was not until the advent of artificial transmutation that such a series was found.^{1,2} This artificially produced decay chain is called the "neptunium series" after Np^{237} , the long-lived parent of the series.

From time to time, individual synthetically made isotopes have been added to these main series as extensions or as one-member branches.

The existence of a branch of the uranium-radium series consisting not of one but of a whole series of isotopes is reported in this paper. The authors propose to call this new series of synthetically made isotopes the "protactinium series," after Pa^{230} , its first member.

The course of the decay of the protactinium series is as follows:

In Fig. 1 the relation of the protactinium series to the uranium-radium series is presented.

2. PRODUCTION OF THE PROTACTINIUM SERIES

The protactinium series was originally produced by a (d,4n) reaction in a 100- μ a-hr bombardment of thorium metal with 22-Mev deuterons and by an (α ,p5n) reaction [with probably some contribution from an (α ,6n) reaction] in a 30- μ a-hr bombardment of thorium metal with 44-Mev helium ions. The bombardments were carried out in the 60-in. cyclotron at the University of California under the direction of J. G. Hamilton.

The type of nuclear reaction in which four to six particles are ejected has been encountered only recently, largely owing to the fact that the rebuilding of the cyclotron and the resultant increase in the energy of the ion beams have made such reactions energetically possible.

Among the first to observe the (d,4n) reaction were James, Florin, Hopkins, and Ghiorso in a bombardment of U^{238} with 22-Mev deuterons.³ The (α ,p5n) and (α ,6n) reactions are probably reported for the first time in this paper.

The protactinium series was subsequently produced by the following reactions: $\text{Pa}^{231}(\text{d},\text{p}2\text{n})\text{Pa}^{230}$ (reference 4), $\text{Pa}^{231}(\alpha,\alpha\text{n})\text{Pa}^{230}$ (reference 4), and $\text{Io}^{230}(\text{d},2\text{n})\text{Pa}^{230}$ (reference 5). The last reaction represents the best method for production of the protactinium series.

3. DISCOVERY OF THE PROTACTINIUM SERIES

The nuclear reactions which produced the protactinium series in the bombardments of thorium metal were accompanied by numerous

other reactions such as (d,n), (d,p), (α ,n), (α ,p), etc. In addition, some deuteron and helium-ion induced fission of the Th^{232} occurred. The resulting mixture of radioactive isotopes complicated the determination of the decay scheme of the new series.

One of the first clues leading to the discovery of the new series was the decay of alpha activity in the pure uranium fraction of the thorium-helium-ion bombardment which indicated the presence of an isotope of uranium with a half life of approximately three weeks. The uranium isotopes which could conceivably be present were those of atomic mass 235 or less; U^{235} , U^{234} , and U^{233} are all so long-lived (10^5 years or more) that they would have shown no change in counting rate. A sample of the 70-year U^{232} (reference 3) should show an increase of about 10 per cent per month from the growth of alpha-emitting daughters. Hence it was necessary to conclude that a new uranium isotope of mass 231 or less was present.

An examination of the alpha-particle energies of the activity in the uranium fraction a few hours after separation revealed the presence of five equally abundant activities with energies greater than that of the U^{232} alpha particle. The growth of the daughters of the uranium isotopes of mass 232 or higher would not be appreciable within a few hours. This is further evidence for a uranium isotope of low mass followed by four daughters with relatively short half lives.

The rate of growth of daughters was determined by observing the increase of alpha activity in a uranium sample very soon after purification. By extracting the uranium into ether and evaporating the ether directly on a platinum plate, it was possible to get the sample to an alpha counter within 6 min after purification. There was an initial rapid growth of alpha activity which essentially reached its maximum (after 4 hr) at a level of activity which was five times the activity present at the time of purification (see Fig. 2). This is further evidence for the presence of four alpha-emitting daughters of the new uranium isotope. A decay curve which is complementary to the exponential growth of Fig. 2 may be obtained by plotting on semilogarithmic paper the difference between the equilibrium counting rate and the observed counting rate as a function of time. A curve obtained in this manner gave a straight line with a half-life period of $\frac{1}{2}$ hr (see Fig. 3). The fact that four alpha emitters grew in with this half life indicates that the first daughter of the uranium, a thorium isotope, has the $\frac{1}{2}$ -hr half life and that the others have considerably shorter half lives. After equilibrium had been reached, the total activity decayed with a half life of three weeks.

When it was found that the uranium fraction from a deuteron bombardment of thorium also contained five distinct alpha activities and

decayed with the same half life as the uranium fraction from the helium-ion bombardment of thorium, the mass number 231 was eliminated from consideration. The fact that a uranium isotope could not be formed directly by a deuteron bombardment of thorium but could only result from the beta decay of a protactinium isotope, together with the fact that Pa^{231} is a long-lived alpha emitter (3.4×10^4 years), justifies this elimination. Therefore the isotope was assumed to be U^{230} .

The next logical step, the search for a uranium daughter in the protactinium fraction, was carried out by isolating a protactinium fraction free from uranium and subsequently extracting a uranium fraction from this after a growth period of several days. The five new alpha activities and a decay of total activity were observed in the uranium fraction so isolated. This experiment was repeated on the protactinium fraction of the thorium-helium-ion bombardment with the same results. This repetition was important since the uranium isotope in the helium-ion bombardment could have been formed directly by an $(\alpha, 6n)$ reaction or indirectly by an $(\alpha, p5n)$ reaction producing Pa^{230} , followed by a beta decay of Pa^{230} . The evidence indicates that an $(\alpha, p5n)$ reaction does occur, but it does not eliminate the possibility of some U^{230} being formed directly by an $(\alpha, 6n)$ reaction. It was calculated that more U^{230} was isolated in the first uranium separation from the thorium-helium-ion target than could be accounted for by Pa^{230} beta decay on the basis of the later growth of U^{230} into the protactinium fraction. This was interpreted as evidence for the occurrence of an $(\alpha, 6n)$ reaction. Five alpha disintegrations starting with U^{230} would produce ${}_{84}\text{Po}^{214}$ which is RaC' of the uranium series (see Fig. 1). The energy of the most energetic of the five unknown alpha emitters is indeed identical within experimental error with the 7.68-Mev energy of the RaC' alpha particle (see Sec. 4.9). If the original protactinium isotope were Pa^{229} or Pa^{228} , the resulting polonium isotopes would be Po^{213} or ThC' with energies (8.28 and 8.776 Mev, respectively) much greater than that of RaC'. [Pa^{229} was subsequently discovered to be a 1.4-day alpha-emitting isotope.⁵] Furthermore, on theoretical grounds, the $(d, 5n)$, $(d, 6n)$, $(\alpha, p6n)$, and $(\alpha, p7n)$ reactions required to produce Pa^{229} and Pa^{228} are not thought to be energetically possible with 22-Mev deuterons and 44-Mev helium ions.

4. EXPERIMENTAL PROCEDURE

The types of chemical operations performed in treating the cyclotron targets and in isolating the uranium and protactinium fractions

are briefly described below. Following this a description is given of the physical measurements and the chemical operations performed on these fractions to identify and characterize the individual isotopes.

4.1 Milling and Dissolving. The cyclotron targets in these bombardments consisted of thorium-metal disks 8 cm in diameter and 5 mm thick. The 25- by 65-mm rectangular area actually struck by the beam was located by inspection and by radiographs. The top layer of metal was removed from this area by clamping the disk in a special covered mount and milling off 0.030 in. The millings, which amounted to 15 g of thorium metal, were dissolved by the addition of 16N nitric acid. The reaction was initiated and kept going at a steady rate by the periodic addition of small quantities of hydrofluoric acid and by the application of heat.⁶

4.2 Separation of a Pure Uranium Fraction. Half of the resulting solution was evaporated to thorium nitrate crystals, taken up in dilute nitric acid, and transferred to a 100-ml Kjeldahl flask where it was saturated with ammonium nitrate to make 30 ml of solution. This solution was shaken with 60 ml of ethyl ether to extract uranium.⁷ The phases were separated by freezing out the aqueous phase with a dry ice-acetone bath and pouring off the ether. The extracted uranium was purified from the small percentages of fission products and thorium accompanying it into the ether layer by shaking the ether layer with three successive 20-ml portions of slightly acidic 10N ammonium nitrate wash solution in 100-ml Kjeldahl flasks. The extracted uranium was stripped from the ether in a final flask containing pure water. The ether was put through the same sequence of operations several more times to ensure complete recovery of the uranium. The final water solution was transferred to a suitable volumetric container from which samples were removed for radioactivity studies and for further chemical treatment.

4.3 Separation of a Pure Protactinium Fraction. With the uranium completely removed by ether extraction it was possible to remove a pure protactinium fraction from the solution left in the first Kjeldahl flask by a quite similar solvent extraction process employing diisopropyl ketone as the solvent.⁸ Thorium, fission products, and other impurities were removed from the ketone layer with wash solutions 3N in ammonium nitrate and 1N in nitric acid. The protactinium was extracted from the ketone with dilute nitric acid solution to ensure the recovery of the protactinium in a state which could be reextracted if necessary. After transferring the protactinium to a suitable volumetric container, samples were removed for radioactivity studies and for further chemical treatment.

4.4 Determination of the Half Life of U^{230} . Samples of U^{230} were prepared by extracting the uranium which had grown into an originally pure protactinium fraction. Several protactinium isotopes besides Pa^{230} were present. Pa^{233} , Pa^{232} , and Pa^{231} were formed in the deuteron bombardment by (d,n), (d,2n), and (d,3n) reactions, respectively. [In the helium-ion bombardment these isotopes were formed by (α ,p2n), (α ,p3n), and (α ,p4n) reactions, respectively. The (α ,p4n) reaction was not specifically observed.] Pa^{231} offered no complications because it is a long-lived alpha emitter. The U^{233} daughter of Pa^{233} is so long-lived (1.62×10^5 years) that the presence of Pa^{233} does not interfere with the preparation of a U^{230} sample. However, it does complicate the characterization of the beta radiation of Pa^{230} since the half life of Pa^{233} (27.4 days) is close to that of Pa^{230} (17 days). This necessitated the indirect determination of this half life as described in Sec. 4.7. The presence of the 1.4-day⁹ Pa^{232} , which decays to a 70-year U^{232} daughter, made impossible the isolation of a uranium sample suitable for the half-life determination of U^{230} as long as it was present. This difficulty was eliminated by letting the protactinium activity decay 16 days. By this time the Pa^{232} had decayed to 0.1 per cent of its original value while the Pa^{230} had decayed by only about half. At the end of this period the uranium was completely removed by repeated ether extraction and discarded. Pure U^{230} was permitted to grow in for a period of one week after which another ether extraction was performed to remove it from the protactinium. Samples of this uranium were mounted on platinum counting disks for the purpose of following changes in alpha activity.

It was early discovered that samples of U^{230} would leave a residual activity in the counter upon removal. This was first thought to be due to an emanation, but experiments to be described (Sec. 4.6) demonstrated that it was due to recoiling nuclei from the energetic disintegrations of U^{230} and its alpha-emitting daughters. This behavior was later found to be very useful (see Secs. 4.5 and 4.8), but in counting samples for the decay of U^{230} it was necessary to consider the danger of erratic results due to loss of recoil atoms. This difficulty was resolved in two ways: (1) by permitting the sample to come to equilibrium in the counter before making a count and (2) by covering the sample with a light film of Zapon to prevent the recoil atoms from escaping.

A U^{230} decay curve is shown in Fig. 4. A least-squares treatment of the data yielded a value of 20.8 days for the half life.

4.5 Identification of Th^{226} and Determination of Its Half Life. It was postulated above from the characteristic growth of alpha activity of a sample of U^{230} (Figs. 2 and 3) that the first daughter of U^{230} (Th^{226})

has a half life of approximately $\frac{1}{2}$ hr. This was shown to be correct by a chemical isolation of the thorium.

The thorium was isolated by coprecipitation with zirconium iodate which is known to be a specific carrier for thorium.² Zirconium nitrate was added to a dilute nitric acid solution of U^{230} in equilibrium with its daughters, and zirconium iodate was precipitated by the addition of iodic acid. The precipitate was dissolved with sulfur dioxide, reprecipitated with iodic acid, and mounted on a counting disk. The rate of decay of alpha activity was determined, and a half life of 31 min was found.

With the Th^{226} positively identified, a more accurate value of the half life was determined by following the decay of recoil activity left in an alpha counter after removal of an active sample of U^{230} (100,000 alpha c/min) which had been in the counter for 1 hr. An initial activity of over 8000 c/min decayed to the background of the counter [any contribution by "aggregate" recoil to the recoil activity must be negligible since no long-lived component due to U^{230} was found in the recoil-atom decay curves] (see Fig. 5). The small amount of short-lived activity indicated by the beginning of the curve was later shown to be due to Ra^{222} . The half life obtained for Th^{226} is 30.9 min. This is slightly greater than the value obtained from analysis of the growth curve (Fig. 3) because in the latter case the approximation was made that the U^{230} activity was constant during the time of growth.

4.6 The Emanation Isotope. It was mentioned above that the 30.9-min contamination of the alpha counter by samples of U^{230} was thought at first to be due to the emanation isotope $_{86}Em^{218}$. However, this was shown not to be the case even before the 30.9-min activity was identified with Th^{226} by the following evidence:

1. Replacing the air in the contaminated chamber did not remove the contamination.
2. Placing in the counter an active U^{230} sample covered with two baffle plates, which permitted the escape of an active gas by an indirect route but offered no direct path for the escape of a recoil atom, did not result in any measurable contamination of the chamber.

These experiments demonstrated that the contamination was due to recoiling nuclei. They do not disprove the existence of an emanation but merely indicate that if it exists it must be short-lived. To set an upper limit on the half life of the emanation, a series of experiments was performed by Fineman, Weissbourd, and Kohman.¹⁰ They arranged to flush the gas emerging from a boiling solution of U^{230} directly into a special alpha-counting chamber. This was done without detecting any counts above background. From their work they set an upper limit of 1 sec for the half life of Em^{218} . This half life was later

determined to be 0.019 sec by Studier by means of an electronic coincidence method.¹¹

This short half life excludes the possibility of chemical identification of Em^{218} , and the evidence for the existence of the isotope is indirect, resting on the over-all evidence for the series and particularly on the identification of its RaC' daughter by energy measurements.

4.7 Determination of the Half Life of Pa^{230} . The direct determination of the half life of Pa^{230} using the protactinium fractions of the thorium bombardments was rendered difficult because of the presence of Pa^{233} . Hence indirect methods were used.

A preliminary value was obtained by extracting and measuring the U^{230} produced in equal periods of time from a sample of protactinium. In this manner a crude half-life value of about two weeks was obtained.

A more accurate value was obtained by mounting a sample of Pa^{230} on a platinum counting disk and following the rate of change of the alpha activity of the sample. Such a growth and decay curve is shown in Fig. 6.

By substituting the half life of U^{230} determined above into the standard growth equation,

$$N_2 = N_{01} \frac{\lambda_1}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

where N_2 = number of U^{230} atoms

N_{01} = number of Pa^{230} atoms initially present

t = time

λ_1 = disintegration constant of Pa^{230}

λ_2 = disintegration constant of U^{230}

theoretical curves for various half lives of Pa^{230} can be calculated and compared with the experimental curves. In this way, using three separate samples, a value of 17.0 ± 0.5 days was determined for the half life of Pa^{230} .

4.8 Identification of Ra^{222} and Determination of Its Half Life. From the failure to observe any alpha activity in a radium fraction that was isolated rapidly by chemical precipitation of a barium chloride carrier from an active solution of U^{230} in equilibrium with its daughters, an upper limit of 1 min was set on the half life of the radium isotope. Although attempts to identify the Ra^{222} chemically were unsuccessful, an alpha-emitting Th^{228} is proof of its existence. It will be recalled that the decay of recoil activity from a U^{230} sample (Fig. 5) indicated the presence of a short-lived component with a half life of the order of $\frac{1}{2}$ min. Since both Em^{218} and RaC' have half lives much shorter

than 1 sec, this activity must be due to Ra^{222} . It was also noted that a sample of Th^{226} leaves a recoil activity in an alpha-counting chamber after the sample is removed, and the decay of this activity was used to determine the radium half life.

To get the maximum amount of recoil from a Th^{226} sample, a sample free from carrier was prepared as follows: A 0.5N nitric acid solution containing about 100,000 c/min of U^{230} was shaken with an equal volume of 0.15M solution of thenoyl trifluoroacetone (TTA) in benzene to extract the Th^{226} from the aqueous solution.¹² The benzene solution was evaporated directly on a platinum counting disk. By inserting this disk in a standard alpha-counting chamber for a few minutes it was possible, because of the recoil phenomenon, to introduce Ra^{222} into the chamber at a rate of several thousand counts per minute. The Th^{226} was then removed, and the recoil activity was measured at intervals of 0.1 min until decay was complete.

It was necessary to measure the activity at such short intervals of time because of the short half life of Ra^{222} , and as a result the statistical fluctuations were rather severe. An integral decay curve was plotted to minimize the scatter of points. The error which would result from the use of the usual differential curve because the duration of each measurement was an appreciable fraction of a half life was also eliminated. By subtracting N_t (the total number of counts up to a given time) from N_∞ (the total number of counts observed on complete decay) and plotting the difference ($N_\infty - N_t$) on a logarithmic scale as a linear function of time, a straight line was obtained, the slope of which determined the half life. Such a curve is shown in Fig. 7. The half life of Ra^{222} based on four such determinations is 38.0 sec.

4.9 Determination of the Alpha Energies of the Members of the Protactinium Series. The energies of the alpha particles were determined with a multichannel differential pulse analyzer.¹³ The instrument which was used has 48 electronic channels which register all the alpha pulses within a selected range of energies. Each channel records only the pulses falling within a narrow energy band; the 48 channels cover 48 continuous energy bands of equal width increasing in energy from channel 1 to channel 48. By plotting the total number of alpha counts per channel against channel number, a peak will be observed for each alpha group. The position and size of the peak measure, respectively, the energy and abundance of the alpha group.

Figure 8 shows the entire series of peaks in the protactinium series. These peaks correspond to U^{230} , Th^{226} , Ra^{222} , Em^{218} , and RaC' . To determine the energies it was necessary to calibrate the instrument with several isotopes whose known energies are approximately

the same as those of the protactinium series. Among these standards was a preparation containing RaC' which served to establish the identity of the most energetic alpha in the protactinium series. With the aid of these standards the unknown energies were estimated to be 5.8_e, 6.3, 6.5, 7.1, and 7.7 Mev.

The question of the assignment of each energy to the proper isotope remained. The RaC' assignment was the only certain one in the beginning. The assignment of the energy of the U²³⁰ alpha particle was made very definite by means of two experiments.

1. An active sample of pure Pa²³⁰ was permitted to decay to U²³⁰ for several days. Then a rapid ether extraction was performed to remove uranium. A sample of the U²³⁰ was quickly inserted in the pulse-analyzer instrument, and the alpha spectrum was measured before the daughter isotopes had time to grow into their equilibrium value. The alpha spectrum was redetermined after several hours when the daughter isotopes were in equilibrium. The 5.8_e-Mev peak, which was prominent in the first curve, was assigned to U²³⁰, and its relation to the other peaks was established by the second curve.

2. In a second experiment a 2-in. aluminum disk was fastened to the upper electrode of a standard alpha-counting ionization chamber and used to collect recoil atoms from a very active sample of U²³⁰ placed on the lower electrode. This disk was quickly removed and subjected to pulse analysis. All peaks except the 5.8_e-Mev peak were present, which confirms the assignment of this peak to U²³⁰.

This leaves three energies to be assigned. A rigorous assignment is made very difficult because of the short half lives and because of the rapidity with which these isotopes come into equilibrium with each other. Experimental methods are known by which such a problem may be solved, but up to the present the necessary instruments have not been available to perform such experiments. Hence the remaining energies have been tentatively assigned to the isotopes in the inverse order of their half lives. Thus the following assignments are made: the 6.3-Mev alpha particle to the 30.9-min Th²²⁸, the 6.5-Mev alpha particle to the 38-sec Ra²²², and the 7.1-Mev alpha particle to the 0.019-sec Em²¹⁸.

5. CROSS SECTIONS FOR THE NUCLEAR REACTIONS

Only rough data were collected on the yields of various nuclear reactions involved in these bombardments. The cross section for the (d,2n) reaction is about 3×10^{-26} cm². The cross section for the sum of the (d,n) and the (d,p) reactions is 2.2 times this value; the ratio of cross sections is known more accurately than the absolute values.

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Fig. 2—Growth of alpha activity in a sample of U^{230} .

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Fig. 3—Complement of the growth curve of a sample of U^{230}

Fig. 4—Determination of the half life of U^{230} from the decay of alpha activity of a sample of U^{230} in equilibrium with its daughters.

Fig. 5—Determination of the half life of Th^{228} by the decay of alpha activity from the recoil atoms of U^{230} .

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Fig. 6—Determination of the half life of Pa^{230} from the growth and decay of daughter alpha decay.

Fig. 7—Determination of the half life of Ra^{222} by the decay of recoil activity from a Th^{226} sample. N_{∞} = total counts observed on complete decay, and N_t = total counts observed to any given time.

Fig. 8—Alpha spectrum of the protactinium series as obtained with a multichannel differential pulse analyzer.

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Paper 9.3

THERMAL-NEUTRON CAPTURE CROSS SECTION OF Th^{230} BY MEASUREMENT OF UY

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1. INTRODUCTION

A preliminary report of these experiments has been given earlier.¹ It was hoped at the time that more accurate measurements could be made later, but, since no experiments of this type have yet been carried out, the preliminary work is reported here. The reaction whose cross section was measured is $\text{Th}^{230}(\text{n}, \gamma) \text{Th}^{231}(\text{UY})$.

The average activation cross section σ of Th^{230} (ionium) may be defined by the equation

$$N_{\text{UY}} = N_{\text{Io}} \sigma nvt \quad (1)$$

where N_{UY} = number of UY nuclei formed throughout the entire bombardment

N_{Io} = number of Io nuclei present

nv = average thermal-neutron flux

t = time of bombardment

As is usual in such measurements, the evaluations of nv and of N_{UY} were subject to the largest errors because of difficulty in neutron-flux measurements and in absolute beta counting.

2. METHOD OF MEASUREMENT

A sample of ionium mixed with Th^{232} was sealed in a quartz tube and irradiated in the thimble of the Chicago heavy-water pile together

with gold-foil monitors. After about a half day of almost steady bombardment at a constant power level, the sample was dissolved, and aliquots were mounted. The decay of these samples was followed until the 25.6-hr UY was gone.² It was continued long enough to evaluate the amount of the 27.4-day Pa²³³ formed through the reaction

The amount of ionium (half life 8.1×10^4 years) in the original sample was determined by making a specific alpha-activity determination. The neutron-flux measurement involved comparison of the activity of the gold-foil monitor with that of a similar monitor activated in the standard pile.

3. MEASUREMENT OF THE AMOUNT OF IONIUM BOMBARDED AND THE AMOUNT OF UY FORMED

Following the bombardment, the sample was dissolved in acid, and known aliquots were evaporated on glass plates. No chemical purification was undertaken since it was felt that very little fission had taken place. This supposition was justified by the fact that the decay curve showed only two components, which were ascribable to the two expected activities, UY and Pa²³³.

In order to evaluate the UY disintegration rate from its counting rate, it was necessary to correct the experimental data by means of the following equation:

$$N'_{\text{UY}} = \frac{1}{\lambda} A'_{\text{UY}} = \frac{1}{\lambda} \frac{A_{\text{UY}} (\text{DS}) (\text{ZA})}{(\text{G}) (\text{BS})} \quad (2)$$

where N'_{UY} = number of UY atoms in one aliquot at the end of bombardment

A'_{UY} = disintegration rate of this aliquot at end of bombardment

A_{UY} = counting rate at bombardment end

DS = fraction of counts due to beta particles (disintegration scheme correction)

ZA = correction of beta-particle absorption curve to zero absorber

G = fractional geometry at the position of the sample

BS = back-scattering correction for the beta particles

To evaluate A_{UY} , the decay of four samples was followed for several weeks with a mica-window Geiger-Mueller tube, at which time it was evident that only Pa^{233} was decaying. Subtracting this component, the residual activity was extrapolated to zero time (end of bombardment). The average of four samples gave $A_{UY} = 14,000 \text{ c/min} \pm 2 \text{ per cent}$ (average deviation).

The geometry at the shelf position at which these measurements were made was calibrated by the use of a secondary UX standard loaned by D. W. Engelkemeir. It was made from uranium oxide and had been calibrated against an essentially weightless sample of UX precipitated from a known amount of "old" uranium and mounted on very thin mica to reduce back-scattering.^{3,4} The geometry value found by using this standard was 0.235.

To evaluate the disintegration rate from the counting rate, it was necessary to determine the number of counts due to UY beta particles, i.e., to determine the correction DS. Absorption and coincidence measurements² have shown that there is apparently a single beta particle (half thickness 6.1 mg/cm^2 in aluminum) followed by several gamma rays, at least one of which is highly converted. Although the data were not accurate enough to fix the disintegration scheme completely, it seems likely that only one beta particle is emitted per disintegration. Thus, without knowing more details of the decay scheme, it is possible to say that of the counts found through 3.20 mg/cm^2 of absorber (including window), 73 per cent represented beta particles of UY. Thus $DS = 0.73$.

Using 6.1 mg/cm^2 as the half thickness of the beta-particle radiation, the correction for the extrapolation of this component to zero absorber was found to be: $ZA = 1.44$.

Because the sample was mounted on thick glass, it was also necessary to correct the beta-particle counting rate for back-scattering. Although the published data⁵⁻⁷ give some information on the amount of back-scattering to be expected, these data apply only to the effect of the back-scattering on the counting rate for finite window thickness. For absolute beta counting, however, it is necessary to know the effective back-scattering on extrapolation to zero absorber. The difference between these two types of back-scattering corrections would be significant only for beta particles as soft as those found here. A discussion of this problem and attempts to evaluate the differences have been reported elsewhere.^{8,9} The conclusion⁹ was that, for samples of low beta energy which were mounted on thick glass, two values for the back-scattering correction might be chosen, depending upon the assumptions made. These values were 1.13 and 1.28. Because the true

back-scattering correction may lie anywhere between these, the calculations will be carried through using both extreme values.

From Eq. 2, the value of N'_{UY} was found to be

$$N'_{UY} = \frac{1}{0.000451} \frac{(14,000) (0.73) (1.44)}{(0.235) (1.13 \text{ or } 1.28)} \quad (3)$$

For $BS = 1.13$ or 1.28 , $N'_{UY} = 1.23 \times 10^8$ or 1.09×10^8 atoms, respectively.

Although the bombarded thorium sample contained $138 \mu\text{g}$, only a part of it was ionium; the remainder was Th^{232} . To determine the fraction of Th^{230} present, the specific activity was measured by determining the counting rate of a known weight of the total thorium. Using the half-life value of 8.1×10^4 years (the mean of available values¹⁰⁻¹²), the ionium concentration was found to be 24.4 per cent by weight. From the aliquot ratios used in dilution of the bombarded sample, each one of the samples measured was found to contain $0.0169 \mu\text{g}$ or 4.4×10^{13} atoms of Th^{230} .

4. NEUTRON-FLUX MEASUREMENT

Following the bombardment, the activity of the gold-foil monitor was measured with a calibrated ionization chamber. The dimensions of the gold foils (1 cm^2 in area and 0.001 in. thick) had been chosen to give high activities without introducing self-absorption. The activation due to resonance absorption was subtracted by the use of a cadmium ratio determined previously,⁸ while a simple calculation showed that, for this thickness of gold, the self-absorption of the thermal-neutron activation only amounted to a few per cent. The chamber had been indirectly calibrated with a gold foil which had been irradiated in the standard pile. [The standard pile is a large rectangular graphite structure, into which a Ra-Be source of known neutron emission can be inserted. The neutron distribution has been calibrated, so that the neutron flux at a number of positions in the pile is well known in terms of the total neutron emission of the source.] The details of the calibration and the corrections required have been discussed elsewhere.^{8,9} The thermal-neutron flux calculated was 1.25×10^{12} neutrons/sec/cm²; the effective neutron temperature was 400°K . The flux value is probably correct to ± 15 per cent.

5. CROSS-SECTION CALCULATION

If N_{UY} represents the total number of UY atoms formed during a steady bombardment, it can readily be shown that

$$N_{UY} = N'_{UY} \frac{\lambda t}{1 - e^{-\lambda t}} = N'_{UY} (1.22) \quad (4)$$

where t (5.53×10^4 sec) was the time of bombardment. From Eqs. 1 and 4 and from the values of N'_{UY} , N_{I_0} , and nv given in Sec. 3, the effective neutron capture cross section of Th^{230} may be calculated as 49 barns (for $BS = 1.13$) or 44 barns (for $BS = 1.28$).

These values may be considered as "effective" values. Since no cadmium ratio was determined, an unknown amount of resonance capture occurred. In addition, the thermal part of the cross section holds for the temperature of the neutrons in the pile (400°K). These questions have been discussed in greater detail elsewhere.^{8,9} If the resonance activation is neglected, the cross section for the monoenergetic neutrons corresponding to a velocity of 2200 meters/sec may be calculated from the relation

$$\sigma_0 = \bar{\sigma}_T \left(\frac{2}{\sqrt{\pi}} \sqrt{\frac{T}{T_0}} \right) \quad (5)$$

where σ_0 = cross section for monoenergetic neutrons at a velocity of 2200 meters/sec

$\bar{\sigma}_T$ = average cross section for neutrons with a Maxwellian energy distribution corresponding to the absolute temperature T

$$T_0 = 293^\circ\text{K}$$

For $T = 400^\circ\text{K}$, σ_0 is 1.32 times $\bar{\sigma}_T$. Thus $\sigma_0 = 65$ barns (for $BS = 1.13$) or 58 barns (for $BS = 1.28$).

6. COMPARISON WITH OTHER MEASUREMENTS

Another measurement has been made by Hyde.¹³ In this measurement, an ionium-thorium sample was bombarded in the pile. The amount of UY formed was determined by isolating and measuring the alpha activity of the Pa^{231} resulting from beta decay. The integrated neutron flux was determined by using the Th^{232} present as a monitor. Absorption of neutrons by Th^{232} gives rise, after a series of beta decays, to U^{233} , whose alpha activity was measured. In addition, a cross-check was obtained by using the second-order reaction involving absorption of neutrons by Pa^{231} . The number of neutrons absorbed by Pa^{231} was measured by determining the alpha activity of the resulting U^{232} , and the flux was determined as before (i.e., from the U^{233} alpha activity).

Using 6.8 barns as the activation cross section of the Th^{232} monitor (see below), the first-order reaction gave 28 barns, while the second-order reaction gave 33 barns. Because of the possibility of losing Pa^{231} in extracting it, Hyde considered his value to be 33 ± 6 barns. Since the value 6.8 barns used for Th^{232} is the cross section for monoenergetic neutrons of 2200 meters/sec velocity, i.e., σ_0 , Hyde's value of 28 barns is also σ_0 provided Th^{230} has no resonance capture. (The amount of resonance capture in ionium is not known.)

In order to compare Hyde's cross-section value resulting from the second-order reaction with his first value, the calculation should be corrected since Hyde used Elson and Sellers' value¹⁴ of 290 barns for the Pa^{231} absorption cross section. This value is an effective average cross section (i.e., disregarding the possibility of resonance capture) for neutrons at the temperature of the pile.¹⁵ Assuming no resonance capture exists, the Pa^{231} value of σ_0 is found to be 450 barns. It should be noted at this point that, if a considerable amount of resonance capture of Pa^{231} exists, the value of 450 barns would be too high since only the thermal part of the cross section would be subject to the calculation used here.^{8,9} However, if the 450-barn value is used, the second-order reaction then gives 21 barns for the σ_0 cross section for Th^{230} . If the 450-barn σ_0 cross section for Pa^{231} is too high, then this value for the Th^{230} cross section is too low. It is suggested, therefore, that Hyde's 28-barn result is the more reliable of his two measurements.

Thus, Hyde's value of 28 barns for σ_0 is to be compared with the values 58 to 65 barns found in the measurements reported here. Evidently, the two methods of measurement gave seriously different results. There are quite a number of possible sources of error in both measurements, and these will now be considered.

As pointed out by Hyde, the two cross sections used by him as standards may have been considerably in error. The Th^{232} cross section has been determined by two different methods with the rather discordant results of 7.6 barns (2200 meters/sec) by the activation method¹⁶ and 6.0 barns by the absorption method (effective pile poisoning).¹⁷ The average value 6.8 barns has been used and is said¹⁸ to have a probable error of ± 20 per cent. The value of 290 barns is subject to a number of possible sources of error and may be off by 30 to 40 per cent⁹ (probably too high). In addition, as pointed out above, the existence of an unknown resonance effect would tend to bring the 2200 meters/sec Pa^{231} cross section down and thus raise the value of the Th^{230} cross section calculated from the second-order reaction.

To make the results of the two experiments give closer agreement, Hyde's value would have to be raised and/or the value calculated in

this paper would have to be lowered. Hyde's results would be raised if the value of the Th^{232} cross section were greater than 6.8 barns and if the value of the Pa^{231} effective cross section were smaller than 290 barns (for the pile). Hyde's low results might also be partially explained by incomplete separation of the protactinium fraction from the neutron-bombarded ionium—the loss could have been as high as 20 per cent.

The sources of error in the present measurement are chiefly in the determination of the UY disintegration rate, since it was unlikely that the neutron-flux value was off by more than ± 15 per cent. The most likely source of a large error is the possibility of not properly allowing for counts due to radiations other than the beta particles. A more complete study of the decay scheme is necessary before this can be done more accurately.

So many assumptions and corrections were involved in both measurements that there is no good basis for preferring either result. In lieu of more accurate work, an average might be taken.

Table 1 shows some cross-section values for Th^{230} , including results from both this and Hyde's paper. The actually measured values were $\sigma_0 = 28$ barns (Hyde) and the average $\bar{\sigma}_T(400^\circ\text{K}) = 46$ barns (this paper); both values involved the assumption of no resonance activation of Th^{230} . Other values are calculated from these two by the use of Eq. 5, again neglecting resonance capture in Th^{230} .

Table 1— Th^{230} Cross-section Values

	This paper	Hyde (Report ANL-4183)
Monoenergetic cross section (σ_0) at 2200 meters/sec, barns	61	28
Effective average cross section for Chicago heavy- water pile [$\bar{\sigma}_T(400^\circ\text{K})$] (neglecting resonance), barns	46	21
Effective average cross section for graphite pile (neglecting resonance), barns	39	18

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Paper 9.4

THERMAL-NEUTRON FISSION PROPERTIES OF Pa^{233}

By French Hagemann, Martin H. Studier, and Albert Ghiorso

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ABSTRACT

The cross section of Pa^{233} for fission with thermal neutrons has been determined to be less than $1 \times 10^{-24} \text{ cm}^2$.

Determination of the thermal- (i.e., cadmium-absorbable) neutron fission cross section of 27.4-day beta-emitting Pa^{233} is complicated by the relatively large cross section for such fission of its daughter U^{233} . Because of this fact it is necessary to achieve a very thorough separation of the Pa^{233} from its uranium daughter and to make fission measurements very quickly following this separation.

The Pa^{233} used in these measurements was obtained from bombardment of Th^{232} with neutrons in the Hanford uranium-graphite pile, according to the reactions

The bombarded thorium metal was dissolved in nitric acid using a small amount of hydrofluoric acid as a catalyst.¹ The excess acidity was partially neutralized with ammonia, and the solution was salted with calcium nitrate to give a final concentration of 5.0N in calcium nitrate, 2.5N in ammonium nitrate, 1.0N in nitric acid, and 1.7N in thorium nitrate. The bulk of the U^{233} was removed by ether extraction,² and Pa^{233} was isolated by a diisopropyl ketone extraction.³ The protactinium was purified further by three manganese dioxide cycles,

each of which involved coprecipitation with manganese dioxide and dissolution of the precipitate with sodium nitrite.⁴ After the third cycle the solution was made 7.0N in calcium nitrate and 1.0N in nitric acid and exhaustively extracted with ether to effect further removal of uranium. The protactinium was again coprecipitated with manganese dioxide, dissolved in concentrated hydrochloric acid, and diluted to an acidity of 0.5N; the protactinium was then extracted into a 0.15M solution of thenoyl trifluoroacetone (TTA) in benzene. TTA has been found to complex protactinium at this acidity;⁵ however, attempts to remove the protactinium from the organic phase by the usual procedure of reextraction with strong acid were unsuccessful. The TTA was therefore destroyed by boiling with aqua regia, the solution was evaporated to dryness, and the residue was dissolved in 9.0N nitric acid. It was found that the protactinium could be extracted from this stock solution by TTA. Since no other element is known to extract with TTA at such high acidity, this seems to be an excellent method of purification. The samples which were used for fission measurements were prepared by extracting the protactinium from portions of the strongly acid solution (9N) with TTA and evaporating the TTA solution directly on the platinum plates which were used for fission counting.

Fission measurements were made in the thermal column of the Argonne heavy-water pile, using the high-sensitivity fission-counting apparatus described by Ghiorso and Bentley.⁶ The fission rate of each sample was compared with that of a standard thin sample of U^{233} measured under identical neutron-flux conditions. The measurements are summarized in Table 1.

The fission cross section of Pa^{233} was calculated from the relation

$$\sigma_{\text{fiss}}(Pa^{233}) = \frac{f(Pa^{233})}{f(U^{233})} \times \frac{\text{wt.}(U^{233})}{\text{wt.}(Pa^{233})} \times \sigma_{\text{fiss}}(U^{233})$$

where $f(Pa^{233})$ and $f(U^{233})$ are the fission-counting rates of the Pa^{233} sample and the U^{233} standard, respectively. The weight of U^{233} on the standard plate was determined by alpha counting. The weight of Pa^{233} present in each sample was calculated from the U^{233} alpha count after essentially complete decay of the Pa^{233} . The value $521 \times 10^{-24} \text{ cm}^2$ was used for the thermal-neutron fission cross section of U^{233} (reference 7). ["Thermal" is used here to indicate those neutrons in the thermal column of the Argonne CP-3 pile.]

Sample 1 in Table 1 was prepared by mounting directly an aliquot of the purified stock solution. Sample 2 was prepared by extracting an aliquot of the stock solution with TTA and mounting the TTA ex-

tract. Sample 3 was prepared similarly to sample 2 except that it was purified further by washing the TTA extract with several portions of 8N nitric acid before mounting.

The apparent cross section of Pa^{233} is seen to decrease with additional purification until, in the case of sample 3, the cross section is zero within the experimental error of the measurements. The upper limit for the Pa^{233} cross section is therefore determined by the maximum error in the measurements. This error was quite large owing to the high background and the relatively small samples employed. It is felt that 15 fission c/min should have been readily detected, which would place an upper limit of about $1 \times 10^{-24} \text{ cm}^2$ on the thermal-neutron fission cross section of Pa^{233} .

Table 1—Fission Measurements on Pa^{233}

Sample	Time since separation from U^{233}	Weight of Pa^{233} , 10^{-8} g	Back-ground	Fission, c/min			U^{233} standard		
				Net	Correction for U^{233} growth	Due to Pa^{233} or U^{233} contamination	Weight, 10^{-8} g	Fission, c/min	$\sigma_{\text{fiss}}(\text{Pa}^{233})$, 10^{-24} cm^2
1	24 hr	3.32	188	234	52	182	2.35	1440	47
2	10 min	2.70	188	12	0	12	2.35	1440	3.8
2	4 hr	2.69	116	28	7	21	2.35	1450	6.6
3	85 min	3.12	520	10	13	<0	2.35	6610	<0

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Paper 9.5

DETERMINATION OF THERMAL-NEUTRON
CAPTURE CROSS SECTION OF Pa^{233}

By Leonard I. Katzin and French Hagemann

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1. INTRODUCTION

Since U^{233} undergoes fission with thermal neutrons with a large cross section,¹ processes for its manufacture have received intensive study. Since neutron production in chain-reacting units requires consumption of fissile material, the process of production of U^{233} is most economical when the minimum wastage of neutrons is allowed. One of the important potential sources of neutron waste in the process is the absorption of neutrons by the intermediate isotope Pa^{233} . In order to assess the magnitude of this source of difficulty, the measurements of the absorption cross section to be described were made.

The synthesis of U^{233} comes about through the following series of reactions:

The half life of the isotope Pa^{233} is so long that even at the end of two months of irradiation with neutrons it still composes half of the reaction product. Thus for the first month or so of irradiation it represents the member of the chain which can be destroyed most readily by neutron reaction. Such destruction is a double loss—the loss of a potential U^{233} atom and the loss of a neutron which if not so absorbed would have reacted with a thorium atom to give a second U^{233} atom through the reaction chain given above.

Although rather long from the neutron-conservation standpoint, the half life of the protactinium isotope is so short that it is impractical

to isolate it for direct measurements of its neutron-absorption cross section. The intense radioactivity of the material (20 gram-equivalents of radium per milligram) and its decay into an isotope with a large capture cross section make a direct determination of absorption cross section by the normal methods rather formidable. This problem has been discussed at some length by Stoughton.²

A type of experiment which Stoughton has not discussed, actually a variant on one of the methods, is described here. A foil of thorium may be irradiated in a high neutron flux for a period which is a fraction of the Pa^{233} half life (e.g., one to two weeks). Within a short time following cessation of the irradiation (e.g., 1 to 2 days) a uranium fraction is separated out from the irradiated material. This uranium fraction will consist of U^{233} formed by decay of Pa^{233} during the bombardment and during the period before completion of the separation. In it will also be a certain amount of U^{234} , formed in one of three manners. Part may be formed through neutron absorption by Th^{233} to give Th^{234} , which eventually decays to U^{234} through Pa^{234} ; part will be formed through absorption of neutrons by Pa^{233} to give Pa^{234} and thence U^{234} ; and part will come from neutron absorption by U^{233} to give U^{234} . The relative proportions from the different sources will be a function of the cross sections for the three capture processes and the irradiation period.

Since the half life of Th^{233} is only 23.5 min, it can be shown (Eq. 2) that half of the maximum amount of this isotope is produced within the first 23.5 min of a constant-intensity irradiation and that about 97 per cent is produced within 2 hr. Furthermore, after about 47 min irradiation there are as many atoms of Pa^{233} present as Th^{233} atoms, and thereafter the ratio of Pa^{233} to Th^{233} increases by approximately unity every 23.5 min. At the end of 24 hr there are about 60 times as many Pa^{233} atoms as Th^{233} atoms. It can be seen that for periods of irradiation on the order of a day or longer, Th^{233} must have a capture cross section much greater than that of Pa^{233} if it is to make a considerable contribution to the U^{234} production. On the other hand, for an irradiation period of the order of two weeks, only 13 per cent of the material has become transformed into U^{233} of known moderate capture cross section, which, averaged over 14 days, corresponds to about 93 to 94 per cent of the material being represented by Pa^{233} during this interval. Accordingly, the experiment essentially is one of irradiating Pa^{233} alone, with probably minor corrections for the other two isotopes which can give rise to U^{234} .

The relation between rate of formation of U^{234} in the U^{233} and the capture cross section of Pa^{233} can be formulated as follows:

$$\frac{dN}{dt} = F[\sigma(\text{Pa}^{233})N(\text{Pa}^{233}) + \sigma(\text{U}^{233})N(\text{U}^{233})] \quad (1)$$

where σ = neutron capture cross section of the indicated isotope present in amount N

F = neutron flux of the irradiation

For an irradiation long enough to make the proportion of material present as Th^{233} very small, it can readily be shown that

$$N(\text{Pa}^{233}) = \frac{k}{\lambda} (1 - e^{-\lambda t}) \quad (2)$$

$$N(\text{U}^{233}) = kt - \frac{k}{\lambda} (1 - e^{-\lambda t}) \quad (3)$$

where k = constant production rate of $(\text{U}^{233} + \text{Pa}^{233})$ under constant flux
 λ = decay constant of Pa^{233}

For mathematical simplicity the negligibly small destruction of Pa^{233} and U^{233} through fission and neutron capture is not introduced into Eqs. 2 or 3. The amount of U^{234} formed can now be obtained by integration. However, what is wanted for the experimental case is the ratio of U^{234} to U^{233} in the sample following separation. To obtain the amount of U^{233} finally present it is necessary to add to Eq. 3 an amount given by the decay of Pa^{233} during the interval p following bombardment until the separation is made.

$$\frac{k}{\lambda} (1 - e^{-\lambda t}) (1 - e^{-\lambda p})$$

The final ratio of U^{234} to U^{233} obtained is then given by

$$\frac{N(\text{U}^{234})}{N(\text{U}^{233})} = \frac{Ft \frac{1}{2}\sigma(\text{U})[\lambda t]^2 + [\sigma(\text{Pa}) - \sigma(\text{U})]\lambda t + [\sigma(\text{Pa}) - \sigma(\text{U})](e^{-\lambda t} - 1)}{(\lambda t) \lambda t - (e^{-\lambda p}) (1 - e^{-\lambda t})} \quad (4)$$

With an irradiation period of 15 days and a period between termination of the irradiation and separation of the uranium of 2.3 days, the values given in Table 1 were calculated. The cross section for capture of U^{233} was taken as $56 \times 10^{-24} \text{ cm}^2$ (reference 1). Table 1 indicates that the principal difficulty in the experiment is the determination of the concentration of U^{234} in the U^{233} .

The direct method of approach to the problem is through mass-spectrographic analysis. However, at the time the problem was undertaken, no method for determining such small amounts of an isotope

differing by only one mass unit in 233 on samples of 100- to 200- μ g weight was available. Other methods were therefore considered.

The similarity of the half lives of U^{233} and U^{234} [1.62×10^5 years (reference 3) and 2.33×10^5 years (reference 4), respectively] and of the energy of their alpha radiations (4.80 and 4.76 Mev, respectively) rendered any simple radioactivity measurements out of the question. One distinctive property in which the two isotopes do differ is in the slow-neutron fission of U^{233} . Accordingly it was the property chosen in which to make the measurements.

If the alpha-particle emission rate of a thin sample preparation of pure U^{233} is measured under specified conditions, and the fission rate of the sample with a specified arbitrary neutron flux is measured, the ratio of the alpha-particle emission rate to the fission rate will be a number characteristic of pure U^{233} when measurements are made under the same arbitrary conditions. If a small amount of U^{234} is now added to the U^{233} sample and the measurements are repeated, the alpha-particle emission rate will be increased in proportion to the amount of U^{234} added, while the fission rate will not be altered. Accordingly, the alpha-to-fission ratio will be increased and will be a number larger than that for pure U^{233} . The ratio of this number to that for pure U^{233} will therefore be greater than 1.00. The quantitative relation between the proportion of U^{234} present and the alpha-to-fission ratio change is developed as follows:

$$\frac{R_2}{R_1} = \frac{\frac{(\lambda_1 m_1 + \lambda_2 m_2)}{f m_1}}{\frac{\lambda_1 m_1}{f m_1}} = 1 + \frac{\lambda_2 m_2}{\lambda_1 m_1} \quad (5)$$

or

$$\left(\frac{m_2}{m_1}\right) = \left(\frac{R_2}{R_1} - 1\right) \frac{\lambda_1}{\lambda_2} = \left(\frac{R_2}{R_1} - 1\right) \frac{T_{1/2}(U^{234})}{T_{1/2}(U^{233})} \quad (6)$$

where R = alpha-to-fission ratio

λ = radioactive disintegration constant

m = mass of material in the sample

f = effective slow-neutron flux

T = half life.

The subscript 1 refers to U^{233} , and the 2 refers to U^{234} .

2. EXPERIMENTAL WORK

A foil of thorium weighing 10 g was prepared from thorium salts which had been freed of uranium impurity to the extent of 1 ppm or

and unknown plates until a total of 52 pairs of measurements was obtained.

Since the gains of the two sets of amplifiers were not identical, a correction was necessary on the apparent fission ratio. This was obtained by measuring a pair of plates and then interchanging their positions and remeasuring. If the apparent fission count ratio is considered as the true fission count ratio times a chamber gain factor, the product of the apparent ratio, upper chamber to lower chamber, for the two measurements should give the square of the gain factor. Division of a given count ratio by the gain factor gives the true fission ratio. Repetition for a number of pairs of plates showed the value of the chamber gain factor, which was about 0.95, to be stable during a day's measurements.

In order to make certain that the standard plates and unknown plates were homogeneous within themselves, intercomparisons of alpha-to-fission ratios were made by direct measurement. It was shown that although about half the plates in each group showed the same alpha-to-fission ratio the rest showed ratios greater than the base group by amounts as high as 1.6 per cent for the extreme. Two factors enter into these variations. The more important is inhomogeneities and self-absorption of fission fragments in even such thin and carefully electroplated samples. A lesser factor may be the differences in the neutron absorption of the backing plates on which the samples are mounted. The differences apparent between plates on direct comparison were confirmed quantitatively by comparing the averages of the several plates of the second group measured against a given plate of either the standard or unknown group. Accordingly, a characteristic correction was given to the alpha-to-fission ratio of each plate.

The magnitude of the net corrections involved and the effect on the counts are shown in Table 2. As can be seen, the scatter of individual values is greatly reduced by these corrections. The root-mean-square deviation from the mean of the 52 measurements is 0.46 per cent, which is about the value which might have been expected from the statistical reliability of the individual factors in calculation of the final alpha-to-fission ratio between standard and unknown (alpha count, 0.2 per cent; fission count, 0.2 per cent; chamber counting ratio, 0.1 per cent). It seems probable therefore that the principal errors have been eliminated and that the figures obtained are a reasonably true representation of the experimental results. These final results give an alpha-to-fission ratio of 1.0018 for the unknown material compared to the standard, with a standard error of 0.0006. It seems, therefore, that the U^{234} content of the high-flux material is significantly

better. The metal foil of 0.8 mm thickness was surrounded by aluminum and encased in an aluminum can. Following 15.0 days of irradiation at almost constant flux in a high-flux column, the thorium foil was separated from the aluminum encasement and dissolved in nitric acid to which a little hydrofluoric acid had been added. When the metal was completely dissolved, calcium nitrate was added to make the solution 5N in that salt, the acidity was adjusted to 0.1N to 1N, and the uranium was extracted in a short packed column with three volumes of diethyl ether.⁵ The procedures to this point were done by remote control behind lead shielding. The activity of the ether extract was sufficiently reduced so that further processing could be done without shielding. Following concentration and further extractions for purposes of purification, 315 μg of U^{233} was obtained; this was estimated to represent about 95 per cent of the U^{233} present at the time of extraction (2.3 days following termination of irradiation).

The purified uranium was then used to make a series of sample plates. Quantities of about 2 μg were electroplated on platinum disks⁶ over an area of 3.5 cm^2 , and the disks were mounted on silver-painted lucite plates for use in the fission counter. A series of counts was made in a high-resolution argon-carbon dioxide alpha counter at 52 per cent counting yield,⁷ and the alpha-emission rate of each plate was determined to 0.1 to 0.2 per cent reliability. A similar set of plates was made from U^{233} produced in the Clinton pile with a longer irradiation at lower flux, followed by complete decay of the Pa^{233} . This second set of five plates was used as a standard in the fission-counting measurements and was compared with the six plates of high-flux-short-irradiation material.

Fission measurements were carried out at the Argonne CP-3 pile, using the thermal-column beam of thermal neutrons. The apparatus consisted of two small lucite fission chambers attached to suitable amplifying and recording devices. The chambers were mounted one over the other, in relatively close proximity, so that the neutron flux at the two chambers was essentially identical.⁷

The measurements consisted in comparing the fission rate of a standard plate in the upper chamber with the rate of an unknown plate in the lower chamber. The counts were taken for 5.12 min using a scale-of-512 circuit, and the equality of counting times was assured by governing both circuits with a single switch. In thus taking the ratio of the counts in the upper chamber to those in the lower, variations of the counting time from the semiarbitrarily selected period have no importance; thus a possible source of error is eliminated. The measurements were repeated with various pairings of the standard

Table 1 --- Relation Between Pa^{233} Neutron Capture Cross Section and Ratio of U^{234} to U^{233} in Product *

Cross section, $\text{cm}^2 \times 10^{24}$	N_{234}/N_{233}
0	0.00046
10	0.00110
20	0.00174
30	0.00238
40	0.00301
50	0.00365
60	0.0043
70	0.0049
80	0.0056
90	0.0062
100	0.0068

*Irradiation, 15 days; post-irradiation decay, 2.3 days.

Table 2 — Comparison of Alpha-to-fission Ratios of High-flux Samples with Standard U^{233}

Crude R (unknown) R (standard)	Corr.	Corrected R (unknown) R (standard)	Crude R (unknown) R (standard)	Corr.	Corrected R (unknown) R (standard)
0.9848	0.011	0.9958	1.0105	-0.011	0.9995
0.9949	0.011	1.0060	1.0123	-0.011	1.0013
1.0062	0.001	1.0072	1.0105	-0.011	0.9995
1.0016	0.001	1.0026	0.9886	0.002	0.9906
1.0074	-0.005	1.0024	1.0034	0.002	1.0054
1.0119	-0.005	1.0069	0.9950	0.000	0.9950
0.9933	0.010	1.0033	1.0097	0.000	1.0097
0.9937	0.010	1.0037	1.0132	-0.010	1.0032
1.0000	-0.002	0.9980	1.0121	-0.010	1.0021
1.0071	-0.002	1.0051	1.0287	-0.016	1.0127
0.9813	0.011	0.9923	1.0222	-0.016	1.0062
0.9914	0.011	1.0024	1.0032	-0.001	1.0022
1.0029	0.000	1.0029	1.0062	-0.001	1.0052
1.0115	-0.013	0.9985	1.0093	-0.013	0.9963
0.9996	-0.001	0.9986	1.0165	-0.013	1.0035
1.0157	-0.016	0.9997	1.0002	0.000	1.0002
1.0095	-0.010	0.9995	1.0070	0.000	1.0070
1.0019	0.000	1.0019	1.0059	0.006	1.0119
1.0016	0.002	1.0036	0.9913	0.006	0.9973
1.0021	0.002	1.0041	1.0037	-0.004	0.9997
1.0132	-0.008	1.0052	0.9999	-0.004	0.9959
1.0038	-0.008	0.9958	0.9876	0.006	0.9936
1.0123	-0.014	0.9983	0.9938	0.006	0.9998
1.0176	-0.014	1.0036	1.0114	-0.010	1.0014
0.9987	0.001	0.9997	1.0029	0.005	1.0079
1.0041	0.001	1.0031	1.0157	-0.007	1.0087

Mean 1.0018

higher than that of the standard, since the difference is equal to three times the standard error (less than 0.3 per cent chance probability).

From Eq. 6 and the half-life values already quoted, it is calculated that the U^{234}/U^{233} ratio is greater by 26 parts in 10,000 than the corresponding ratio for the standard material. From Eq. 4 an apparent capture cross section of approximately $34 \times 10^{-24} \text{ cm}^2$ may be calculated. A correction must be made, however, for the U^{234} content of the standard material, which may affect the results. Using Eq. 4, assuming a capture cross section for Pa^{233} equal to that of U^{233} , and applying the conditions under which the standard material is produced at the Oak Ridge National Laboratory (approximately five months of irradiation followed by essentially complete decay of the Pa^{233}), it is calculated that not more than two parts in ten thousand of U^{234} may be expected in the U^{233} . It can also be shown that the reduction in flux through the thorium test foil due to neutron absorption is less than 1 per cent and can therefore be neglected. The corrected ratio of U^{234} to U^{233} for the samples is therefore 0.0028, and the corresponding slow-neutron capture cross section is $37 \pm 14 \times 10^{-24} \text{ cm}^2$.

It is hoped that recent advances in mass-spectrographic technique will facilitate a check of these measurements in a direct fashion.

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Paper 9.6*

A NEW ISOTOPE OF PROTACTINIUM: Pa^{229}

By E. K. Hyde, M. H. Studier, H. H. Hopkins, Jr., and A. Ghiorso

The known isotopes of protactinium include Pa^{234} (UX_2), Pa^{233} ,^{1,2} Pa^{232} ,³ and the recently discovered Pa^{230} .⁴ Evidence has been found for a new isotope of protactinium, Pa^{229} , produced by the reaction $\text{Io}^{230}(\text{d},3\text{n})\text{Pa}^{229}$.

A 35-mg sample of the dioxide of an ionium-thorium mixture (26.4 per cent Io^{230} , 73.6 per cent Th^{232}) was bombarded with 70 $\mu\text{a-hr}$ of 22-mev deuterons in the Berkeley 60-in. cyclotron by Dr. Hamilton and his colleagues.

The dissolution of the target and the separation of a protactinium fraction by diisopropyl ketone extraction were done in a manner very similar to that described elsewhere.⁴

A search in the protactinium fraction for unidentified activities that might be due to Pa^{229} and Pa^{228} revealed the presence of a previously unknown α emitter. The decay of this activity could not be followed directly because U^{230} and its daughters were growing into the protactinium fraction.[†]

However, it was possible to follow the decay of the unknown activity by making frequent measurements of the α -ray spectrum of the protactinium fraction with a pulse analyzer⁵ and by following the decay of the unknown peak. From such measurements a half life of 1.4 ± 0.4 days was determined. The energy of the α particle, determined by the relation of its peak in the α spectrum to the peaks of the protactinium series, was estimated to be 5.4 mev.

*This paper is reproduced direct from "The Transuranium Elements," edited by Glenn T. Seaborg, Joseph J. Katz, and Winston M. Manning, National Nuclear Energy Series, Division IV, Volume 14B, McGraw-Hill Book Company, Inc., New York, 1949. In that volume it appears as Paper 19.17.

[†]The U^{230} resulted from the β decay of the Pa^{230} formed during the bombardment by the reaction $\text{Io}^{230}(\text{d},2\text{n})\text{Pa}^{230}$, as well as by the reaction $\text{Th}^{232}(\text{d},4\text{n})\text{Pa}^{230}$.

The mass assignment was made by isolating and identifying isotopes of the neptunium ($4n+1$) series⁶ from an initially pure protactinium fraction 1 or 2 days after the protactinium fraction had been isolated. Alpha emission of Pa^{229} produces Ac^{225} and thus gives rise to the whole neptunium series below Ra^{225} . Hence the identification of those products is proof for the mass assignment. The amount of Ac^{225} that would have grown into the protactinium fraction from the Pa^{233} [present owing to the nuclear reaction $\text{Th}^{232}(\text{d},\text{n})\text{Pa}^{233}$] was calculated and found to be entirely negligible.

The experimental evidence for the isotopes of the neptunium series was obtained as follows: An aliquot of the protactinium fraction was made 1N in HF, and lanthanum fluoride was precipitated by the addition of 1 mg of lanthanum nitrate. This precipitation is known to carry actinium in good yield but not protactinium. When this fluoride precipitate was slurried onto a platinum plate, it showed the behavior, characteristic of Ac^{225} , of growing in α activity with a half-life period of 5 min immediately after flaming the plate to red heat to drive off the volatile 87^{221} . The α count grew from 2,200 counts per minute to 2,900 counts per minute with a 5-min period changing over into an approximately 45-min period as Bi^{213} grew in. A recoil-atom activity amounting to 56 counts per minute, which was left in the α counting chamber after the sample was removed, decayed with the 5-min half life of 87^{221} .

The lanthanum fluoride precipitate was dissolved in concentrated nitric acid, evaporated to dryness, and taken up in dilute nitric acid. From this solution Bi^{213} was separated by coprecipitation of lead sulfide when 0.5 mg of lead nitrate and hydrogen sulfide were added. The α count of the sulfide sample decayed from an initial 280 counts per minute to 3 counts per minute with a half life of 45 ± 3 minutes. These α particles resulted from Po^{213} , disintegrating at a rate determined by the rate of formation from its 47-min β -emitting parent, Bi^{213} .

From theoretical considerations it is expected that the α decay of Pa^{229} is paralleled by an electron-capture decay. The low energy of the Pa^{229} α particle was unexpected because of its 1.4-day half life, and this may indicate that the true α half life is considerably longer. It was not possible to prove this by observing a 1.4-day x-ray decay in samples of the protactinium fraction because the Pa^{229} activity was masked by a high background from the Pa^{232} , Pa^{233} , and Pa^{230} radiations. The Pa^{232} , in particular, made the measurements almost impossible because of the near identity of the Pa^{232} and Pa^{229} half lives.

The nuclear reaction $\text{Th}^{232}(\text{d},2\text{n})\text{Pa}^{232}$ occurred with a cross section of 4×10^{-27} sq cm in this bombardment; the reaction $\text{Io}^{230}(\text{d},3\text{n})\text{Pa}^{229}$

occurred with a cross section of only 0.24×10^{-27} sq cm, assuming that Pa^{229} decays solely by α emission. Since the cross-section data now available for bombardments of heavy nuclei with 22-mev deuterons indicate that (d,2n) and (d,3n) reactions should occur with approximately equal cross sections, the low value of this second figure may be taken as evidence for branching decay of Pa^{229} by orbital-electron capture.

No evidence was found for the unknown isotope Pa^{228} , which is undoubtedly formed in the bombardment by the nuclear reaction $\text{Io}^{230}(\text{d},4\text{n})\text{Pa}^{228}$.

SUMMARY

A new isotope of element 91, Pa^{229} , has been produced by the nuclear reaction, $\text{Io}^{230}(\text{d},3\text{n})\text{Pa}^{229}$. This isotope emits α particles of 5.4-mev energy with an apparent half life of 1.4 ± 0.4 days. It is believed that Pa^{229} decays principally by orbital-electron capture, but the x rays were not detected because of conflicting activities.

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Paper 9.7

DETERMINATION OF THE HALF LIFE OF IONIUM

By Earl K. Hyde

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The thorium isotope of mass 230, called ionium, is present in all uranium ores because it is a member of the uranium decay chain. Ionium isolated from these ores is always contaminated with thorium-232. Hence the determination of the half life of pure ionium by measurements of naturally occurring ionium involves a determination of the isotopic composition as well as the determination of the specific disintegration rate of the sample.

The presently accepted value of the ionium half life was determined by Curie and Cotellet,¹ who measured the rate of growth of radium into a mixed sample of ionium and thorium, the isotopic composition of which had been determined gravimetrically by Hönigschmid and Horowitz.² The radium was measured indirectly by measuring the radon in equilibrium with it. The value so determined was 8.23×10^4 years; the limit of error was set at 3 per cent.

This paper reports a redetermination of the ionium half life, measuring directly the specific alpha disintegration rate of an ionium-thorium mixture whose isotopic composition had been determined by mass-spectrographic analysis. The value obtained in these experiments was $8.0 \pm 0.3 \times 10^4$ years.

This determination would not have been possible without the mass-spectrographic measurements of Wilfred Rall and A. J. Dempster.

EXPERIMENTAL WORK

The ionium sample was purified by a number of precipitations including a hydroxide precipitation with ammonia and an oxalate pre-

cipitation from 1N nitric acid. The final purification was carried out by repeated extraction with diethyl cellosolve from an aqueous solution 10N in ammonium nitrate and 1N in nitric acid.³ The ionium was removed from the diethyl cellosolve with distilled water. This extraction effects excellent purification of thorium from traces of all impurities⁴ except one or two of the heavier element nitrates which are removed by the previous precipitations.

A portion of the purified ionium was given to Wilfred Rall and A. J. Dempster, who determined the isotopic composition in the mass spectrograph. In nine separate trials using a direct electrometer comparison of the ions collected, they obtained a best value of 26.4 ± 1.1 per cent for the atom per cent of ionium in the sample. Their determination is described in detail elsewhere.⁵

The main portion of the purified sample was transferred to a small platinum crucible, precipitated as oxalate, and ignited at 700°C to convert the oxalate to the dioxide. The crucible was weighed and the oxide dissolved in concentrated nitric acid containing 0.01N HF (reference 6) and transferred to a weighed 10-ml mixing cylinder. The crucible was reignited and reweighed. The solution was diluted to 10 ml with water and perchloric acid to make a solution 5N in perchloric acid. After reweighing the mixing cylinder, weighed aliquots of this solution were removed and diluted to 10 ml with 5N perchloric acid. Weighed aliquots of the dilution solutions were mounted on 1-in. quartz disks by means of the gravimetric aliquoting method described by Westrum.⁷ These samples were counted in several pulse ionization alpha-counting chambers, and a counting-yield factor of 52 per cent was applied.⁸ The contribution of the Th^{232} alpha particles to the total alpha count was entirely negligible.

The specific-activity determination was checked in the following manner. The ionium was precipitated from the perchloric acid solution as the oxalate, redissolved by passing SO_2 into an aqueous suspension of the oxalate, reprecipitated as the hydroxide, and dissolved in nitric acid. Ammonium nitrate was added to this acid solution, and the ionium was extracted with redistilled diethyl cellosolve. The specific activity of this repurified ionium was redetermined in exactly the same manner as described above.

All data and calculations are summarized in Tables 1 and 2.

The average value of the half life derived from the two specific-activity determinations is 8.05×10^4 years. The accuracy of this value is limited principally by the error associated with the mass-spectrographic analysis. The specific-disintegration-rate determination is accurate to within 0.5 per cent, while the standard error associated with the isotopic composition is 4 per cent. In addition, some uncer-

tainty is attached to the use of a counting-yield factor of 52 per cent for the ionium samples mounted on quartz since this factor has not been directly determined for this combination.⁸

This redetermination of the ionium half life agrees, within experimental error, with the value reported by Curie and Cotellet.¹ The fact that these two completely independent methods yield the same value increases the confidence with which the value may be accepted.

Table 1 — Data for First Specific-activity Determination

Wt. of dioxide, mg	6.91			
Wt. of solution, g	13.311			
Wt. of aliquot, g	0.1336	0.1337		
Wt. of dilution solution, g	12.991	12.665		
Wt. of aliquot of dilution solution, g	0.0647	0.0641	0.0632	0.0633
Disintegrations per minute in aliquot	3417	3388	3442	3446
Calculated specific activity, dis/min/ μ g	11,270	11,290	11,310	11,300
Average value of specific activity, dis/min/ μ g	11,290			
Ionium in sample, %	26.4			
Calculated specific activity of pure ionium, dis/min/ μ g	42,770			
Half life of ionium, yr	8.07×10^4			

Table 2—Data for Second Specific-activity Determination

Wt. of dioxide, mg	5.45			
Wt. of solution, g	13.681			
Wt. of aliquot, g	0.1346	0.1357		
Wt. of dilution solution, g	12.905	12.834		
Wt. of aliquot of dilution solution, g	0.0635	0.0637	0.0623	0.0632
Disintegrations per minute in aliquot	1368	1390	1344	1374
Calculated specific activity, dis/min/ μ g	11,370	11,510	11,220	11,320
Average value of specific activity, dis/min/ μ g	11,360			
Ionium in sample, %	26.4			
Calculated specific activity of pure ionium, dis/min/ μ g	43,000			
Half life of ionium, yr	8.03×10^4			

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Paper 9.8

PRODUCTS OF DEUTERON AND HELIUM-ION BOMBARDMENTS OF Pa^{231}

By D. W. Osborne, Roy C. Thompson, and Q. Van Winkle

[Editor's Note: Contribution from the Argonne National Laboratory.]

1. INTRODUCTION

During October 1945, there became available in the Argonne National Laboratory sufficient Pa^{231} to permit cyclotron bombardments to produce and study a number of isotopes near Pa^{231} on the isotope chart. The isotopes in the region of Pa^{231} which were known at the start of this work are shown in Fig. 1. It was expected that bombardment with 22-Mev deuterons would produce the known protactinium isotopes Pa^{232} , Pa^{230} , and Pa^{229} by (d,pxn) reactions, the known uranium isotopes U^{232} and U^{230} by decay of Pa^{232} and Pa^{230} as well as by (d,xn) reactions, and perhaps activities which could be assigned to the unknown isotopes U^{231} and U^{229} . No neptunium isotopes were expected since U^{232} and U^{230} are alpha emitters, and any uranium isotopes with masses of 231 or less would not be expected to decay by beta emission. Bombardment with 44-Mev helium ions was expected to produce the same protactinium isotopes as in deuteron bombardment (except Pa^{232}) by $(\alpha,\alpha xn)$ reactions, the same uranium isotopes (plus undetectable amounts of long-lived U^{233} and U^{234}) by decay and by (α,pxn) reactions, and Np^{234} and perhaps unknown neptunium isotopes of mass less than 234 by (α,xn) reactions.

2. EXPERIMENTAL WORK

The Pa^{231} used in these experiments was concentrated from uranium ores and residues, some of it by members of the Argonne National Laboratory¹⁻³ and some by A. Von Grosse and M. S. Agruss.⁴ All the

Pa^{231} was highly purified in the Argonne laboratory by procedures which included repeated ether extractions of dilute nitric acid solutions salted with ammonium nitrate to remove traces of uranium and extractions of protactinium from 6N to 8N HNO_3 solution with diisopropyl ketone, followed by several washes of the ketone with 1N HNO_3 and then precipitation of the protactinium with hydrogen peroxide solution.

The precipitated protactinium was dissolved in hydrofluoric acid, put on a small platinum interceptor target (0.85-cm² area) by evaporation of the solution to dryness in small portions, ignited to the oxide, and covered with approximately 4 mg/cm² of aluminum foil. The bombardments were carried out by J. G. Hamilton and coworkers with the Berkeley 60-in. cyclotron. In the first bombardment, 2 mg of Pa^{231} was bombarded with 452 $\mu\text{a-hr}$ of deuterons over a period of 8 days; then 4 mg of Pa^{231} was bombarded with 179 $\mu\text{a-hr}$ of helium ions over a period of 15 days, and finally 8 mg of Pa^{231} was bombarded with 239 $\mu\text{a-hr}$ of deuterons over a period of 4 days. At a later date, to look for U^{229} , two short bombardments with helium ions were made and worked up by two of the authors (Osborne and Thompson) at the University of California Radiation Laboratory.

For all the bombardments the maximum energies of the helium ions and of the deuterons were slightly less than the 44-Mev and 22-Mev values originally expected. The maximum energies were 42 and 21 Mev for helium ions and deuterons, respectively, as determined by the range of the alpha particles in air, and the energies of the maximum number of helium ions and deuterons as determined by absorption in aluminum were 38 and 19 Mev, respectively.⁵

Each of the first three targets was returned to this laboratory as quickly as possible, and uranium and protactinium fractions were isolated chemically from the deuteron-bombarded material, and neptunium, uranium, and protactinium fractions from the material which had been bombarded with helium ions. The first fraction was isolated 1 to 1½ days after the end of the bombardment. Aliquots of the fractions were evaporated on platinum foils 0.005 cm thick for studying the alpha activities by decay measurements and by means of the differential alpha-pulse analyzer⁶ and for studying the Geiger-Mueller activities by decay and absorption measurements.

Decay and absorption measurements were also made on samples of unbombarded Pa^{231} under the identical conditions used for measurements on the protactinium fractions from the bombardments in order to enable corrections to be made for the appreciable Geiger-Mueller activity of the Pa^{231} in these fractions. The amounts of Pa^{231} in the smaller protactinium samples were determined by alpha counting.

The decay and absorption curves were usually determined with two or three samples varying in activity in steps of approximately tenfold, and the curves were normalized to one sample by means of ratios of the activity taken at suitable times or with suitable absorbers. Beta and x-ray standards were counted in each series of measurements, and corrections were made for variations in the counting rate of the standards. Corrections were also made for coincidence losses. Absorbers were placed as near as possible to the counter window to minimize the counting of scattered components.

The instruments used for alpha counting were: an atmospheric alpha counter in conjunction with a linear amplifier and scaler, an argon-carbon dioxide fast counter,⁷ and a methane proportional counter.⁸ Geiger-Mueller activities were determined with end-window brass-wall counters with mica windows of 3.3 to 3.8 mg/cm² thickness and usually a filling of ethyl alcohol at 1 cm Hg and argon at 9 cm Hg.⁹ Xenon-filled counters were used in obtaining decay and some absorption curves of the neptunium fraction in the first helium-ion bombardment. Each counter was provided with a shelf arrangement for holding samples and absorbers at standard distances from the window. The body of the counter was surrounded by a close-fitting cylindrical sheath of lead 1.2 cm thick, and the counter assembly was enclosed in an aluminum-lined housing with lead walls 5 cm thick. A Neher-Harper quenching circuit and a Cyclotron Specialties scaler were used with the Geiger-Mueller counters.

3. CHEMICAL PROCEDURES

The procedure used to isolate the uranium and protactinium fractions in the deuteron bombardments will now be described briefly. It was necessary to destroy carbonaceous material on the target, which perhaps came from the oil diffusion pumps of the cyclotron, by fuming the material with nitric and perchloric acids, or better, by ignition in a muffle furnace at 750°C for about 40 min. The material was removed from the target by a combination of scraping and dissolving in concentrated hydrofluoric and nitric acids. The solution was evaporated to dryness, a little concentrated hydrofluoric acid was added, and the solution was evaporated nearly to dryness, so that a trace of fluoride remained to aid in holding the protactinium in solution. The residue was then dissolved in a few milliliters of 2N HNO₃. A portion of this solution was saved, and the remainder was transferred to a small Kjeldahl flask, where solid ammonium nitrate was added to make a solution approximately 1N in HNO₃ and 9N to 10N in NH₄NO₃. Uranium was extracted from this solution by a technique which is standard in the Argonne laboratory. Four to six double-volume por-

tions of diethyl ether were used; sufficient nitric acid was added before each extraction to keep the acid concentration 0.1N or higher. The layers were separated by freezing the aqueous layer with solid carbon dioxide and acetone and pouring off the ether layer. Each portion of ether was shaken with two or three wash solutions containing 0.1N HNO_3 and 9N to 10N NH_4NO_3 , and finally the washed ether was stripped of uranium by means of water (a fresh portion of water was used for each portion of ether). The water extracts, combined and evaporated to a small volume, constituted the uranium fraction. The protactinium was separated from the fluoride and the large concentration of ammonium nitrate by precipitating it twice with sodium hydroxide or ammonia and washing several times with water. The protactinium hydroxide was dissolved in 10 ml of 6N HNO_3 per milligram of protactinium, and the protactinium was extracted by two or three approximately equal-volume portions of diisopropyl ketone which had previously been shaken with an equal volume of 6N HNO_3 . The diisopropyl ketone layers were shaken with two washes of water or 1N HNO_3 and then shaken with a wash of 3 per cent H_2O_2 solution to precipitate the protactinium. The solution of this protactinium peroxide in concentrated nitric acid constituted the protactinium fraction.

Quite often it was desired to isolate protactinium and thorium daughters from the uranium fraction, and the following procedure was generally used. The solution was made 1N in HNO_3 and 9N to 10N in NH_4NO_3 . Uranium was extracted by using several portions of diethyl ether and was set aside for repetition of the isolation of daughters at a later time. Then protactinium was extracted by means of diisopropyl ketone. After removal of uranium and protactinium from the aqueous layer, thorium was coprecipitated on zirconium iodate. The bulk of the carrier was reduced by dissolving the iodate precipitate and precipitating a small amount of lanthanum fluoride, which carried the thorium.

The chemical procedure for the material bombarded with helium ions included separation of a neptunium fraction. After ignition to destroy carbonaceous matter and after removal of the material from the target by scraping and dissolving in hydrofluoric and nitric acids, the solution was evaporated just to dryness, and the residue was taken up in dilute nitric acid. Sodium bromate was added and the solution heated at 100°C for 10 min to oxidize neptunium to Np(VI). A combined neptunium and uranium fraction was then separated by ether extraction, following the same procedure used to isolate the uranium fraction in the deuteron bombardments. The uranium-neptunium fraction was evaporated to dryness with concentrated hydrochloric acid to convert the nitrates to chlorides and was then dissolved in

dilute hydrochloric acid. Ammonium iodide and hydrazine hydrochloride were added to reduce the neptunium to Np(IV), and the solution was then diluted. Neptunium was extracted from this solution with thenoyl trifluoroacetone (TTA) in benzene and then reextracted into hydrochloric acid. The uranium remained in the hydrochloric acid solution and was purified further from neptunium by an additional extraction. A protactinium fraction was separated by the method used for the deuteron bombardments.

4. RESULTS OF DEUTERON BOMBARDMENTS

4.1 Pa^{232} . The decay of the protactinium fractions was followed with a mica-end-window Geiger-Mueller counter through various combinations of absorbers: no absorber; 2.0 g/cm^2 of beryllium (to absorb the beta radiations); 2.0 g/cm^2 of beryllium plus 60 mg/cm^2 of lead (to absorb the beta rays and L x-rays); and 2.0 g/cm^2 of beryllium plus 5.1 g/cm^2 of lead (to absorb all but the hard gamma radiation). After correction for the Geiger-Mueller activity of Pa^{231} and its daughters, as determined by measurements on unbombarded Pa^{231} under the same conditions, the decay curves could be resolved into two half lives, 31 to 36 hr (average, 33 hr) and 17.7 days, which are attributed to Pa^{232} and to Pa^{230} , respectively. Figure 2 shows one of these decay curves. The value of 33 hr for the half life of Pa^{232} is in satisfactory agreement with Jaffey and Hyde's more accurate value of 31.7 hr.¹⁰

The radiations of the 33-hr activity were characterized by absorption curves in lead, with 2.0 g/cm^2 of beryllium covering the sample, and by absorption curves in aluminum. These curves were obtained as soon as possible after separation of the protactinium fraction, and corrections were made for Pa^{230} by comparison with curves obtained on the same samples 9 days later (Figs. 7 to 10), when the 33-hr activity was much smaller than the 17.7-day Pa^{230} activity. Corrections for Pa^{231} were determined by means of absorption curves on samples of unbombarded Pa^{231} obtained at the same time under exactly the same conditions.

The absorption curve in lead, with 2.0 g/cm^2 of beryllium covering the sample, is given in Figs. 3 and 4. After correction for Pa^{230} and Pa^{231} the curve can be resolved into a hard gamma-ray component of half thickness 10.1 g/cm^2 (1.02 Mev), a softer gamma ray of half thickness 0.80 g/cm^2 (0.21 Mev), and a component with a half thickness of 11 mg/cm^2 (23 Kev). The last component is probably a mixture of L x-rays, which have energies of 13.5 to 20.2 Kev for uranium. No K x-rays, which would be expected from decay of 1.4-day Pa^{229} by K electron capture, were found, although 5 c/min might not have been

resolved. The abundances and energies of the radiations are in satisfactory agreement with those observed by Jaffey and Van Winkle¹¹ from a sample of Pa^{232} which was not accompanied by any other activity in appreciable amount.

The absorption curve in aluminum is given in Figs. 5 and 6. This curve was obtained 25 hr before the beryllium-plus-lead curve shown in Figs. 3 and 4; it was obtained on the same samples and under the same conditions. The tube had a 3.76 mg/cm^2 window, and the samples were at a distance of 3.69 cm below the window. The curve can be resolved into a hard component; L x-rays; a soft beta particle or conversion electron (assuming an initial half thickness of 33 mg/cm^2 and a range of about 150 mg/cm^2 , corresponding to a maximum energy of about 480 Kev, in agreement with Jaffey and Van Winkle¹¹); a soft beta particle with an initial half thickness of 6.9 mg/cm^2 , a range of about 70 mg/cm^2 , and an energy of about 280 Kev; and a very soft beta particle or conversion electron with an initial half thickness of about 1.9 mg/cm^2 , a range of about 16 mg/cm^2 , and an energy of about 90 Kev. These results are in reasonable agreement with those of Jaffey and Van Winkle¹¹ except that they did not observe the 90-Kev beta particle. It is not known at present whether this component is a spurious scattered component arising from the geometry or whether it is a beta particle or conversion electron from some other isotope such as Pa^{229} . Data were not available from the other deuteron bombardment to check this curve.

The yield of Pa^{232} was estimated from the counts per minute of the 330-Kev beta particle obtained from resolution of the Pa^{232} aluminum absorption curve, assuming one 330-Kev beta particle per disintegration and using a back-scattering factor¹² of 1.60. From the yield estimated in this manner the cross section for the formation of Pa^{232} by the reaction $\text{Pa}^{231}(\text{d},\text{p})\text{Pa}^{232}$ was calculated to be $40 \times 10^{-27} \text{ cm}^2$ in the first deuteron bombardment and $60 \times 10^{-27} \text{ cm}^2$ in the second bombardment.

4.2 Pa^{230} . Alpha-pulse analyses soon after separation of the protactinium fraction showed Pa^{231} and a small amount of alpha activity that was due to the U^{230} decay series,¹³ but no other alpha activity was observed. Repetition of the pulse analyses at later dates showed that the U^{230} series had grown into the protactinium fraction, establishing the presence of beta-emitting Pa^{230} .

The half life of Pa^{230} was determined by following the decay of the Geiger-Mueller activity in the protactinium fraction and also in samples of unbombarded Pa^{231} through various absorbers. The best value is 17.7 ± 0.5 days from the decay through 2.0 g/cm^2 of beryllium plus 5.1 g/cm^2 of lead (Fig. 2), the combination of absorbers through

which the fraction of the activity which was due to Pa^{231} was least. A concordant value has been obtained by Studier and Hyde,¹³ who followed the growth and decay of the alpha activity in samples of Pa^{230} from deuteron bombardment of Th^{232} . From these measurements they calculated a half life of 17.0 ± 0.5 days for Pa^{230} . Because of the abundant presence of Pa^{233} they were unable to obtain the half life by direct decay or to study the radiations of Pa^{230} .

The radiations of Pa^{230} were characterized by absorption curves obtained after the Pa^{232} had decayed until it was nearly negligible. The absorption of the Pa^{230} radiations in lead with 2.0 g/cm^2 of beryllium covering the sample is shown in Figs. 7 and 8. After correction for Pa^{231} and for Pa^{232} (from Figs. 3 and 4, allowing for 9 days of decay) the curve can be resolved into a gamma-ray component with a half thickness of 9.4 g/cm^2 (0.94 Mev), a gamma ray with a half thickness of 245 mg/cm^2 (74 or 131 Kev, probably 100-Kev K x-rays), and a softer component with a half thickness of 10.8 mg/cm^2 (23 Kev, probably L x-rays). This curve agrees within experimental error with a beryllium-plus-lead absorption curve obtained on a protactinium sample from the first deuteron bombardment which was repurified chemically after decay of the Pa^{232} .

In Figs. 9 and 10 is shown the aluminum absorption curve of Pa^{230} . After correction for Pa^{231} and for Pa^{232} (from Figs. 5 and 6, allowing for 9 days of decay) the curve can be resolved into a hard gamma component (a mixture of the 0.94-Mev gamma ray and the K x-rays found in the beryllium-plus-lead curve), L x-rays (79 mg/cm^2 half thickness, 14.6 Kev), a beta component with a range of about 130 mg/cm^2 (430 Kev), a beta component with an initial half thickness of 14 mg/cm^2 and a range of about 50 mg/cm^2 (220 Kev), and a softer beta component (possibly spurious) with a range of about 13 mg/cm^2 (about 80 Kev). An aluminum absorption curve obtained on a sample of protactinium from the other bombardment which was repurified after decay of the Pa^{232} did not show the softest beta component but otherwise agreed within experimental error.

The abundances of the various components found in the beryllium-plus-lead and aluminum absorption curves may be compared with the number of Pa^{230} beta disintegrations per minute determined from the growth of U^{230} . The curves shown in Figs. 7 through 10 have been normalized to a sample in which there were 1.01×10^4 Pa^{230} beta disintegrations per minute at the time the curves were determined. The geometry was 4.2 per cent. The results are shown in Table 1, together with the back-scattering factors and counting efficiencies used in calculating the abundances. The K x-rays have been corrected to zero absorber assuming a half thickness of 5.0 g/cm^2 in beryllium.

The softest component has not been included in the table. It appears from these data that there are 9 K x-ray quanta emitted per beta disintegration, indicating that decay of Pa^{230} by capture of a K electron is 9 times as frequent as decay by beta emission. A more reliable value of 10 for the K electron/beta branching ratio of Pa^{230} has been determined by Studier and Bruehlman¹⁴ by comparing the yields of Th^{230} and of the U^{230} series growing into a large sample of Pa^{230} from deuteron bombardment of Th^{232} . The present data indicate that the 0.94-Mev gamma ray is associated with the decay by K capture and that there is one 220-Kev beta per disintegration to U^{230} .

To calculate the cross section for the reaction $\text{Pa}^{231}(\text{d}, \text{p}2\text{n})\text{Pa}^{230}$, the value of 10 for the K electron/beta branching ratio of Pa^{230} was used with observations of the growth of the U^{230} series into the protactinium fraction. A cross section of $23 \times 10^{-27} \text{ cm}^2$ was obtained in the first deuteron bombardment and $37 \times 10^{-27} \text{ cm}^2$ in the second bombardment.

4.3 Pa^{229} . Other observers^{15, 16} have produced this isotope by the reaction $\text{Th}^{230}(\text{d}, 3\text{n})\text{Pa}^{229}$ and have observed a peak due to this isotope in alpha-pulse analyses. This peak decays with a half life of 1.4 ± 0.4 days according to the first observations¹⁵ and 1.5 ± 0.1 days according to later work.¹⁶ It has been estimated, mainly from consideration of yields, that Pa^{229} decays approximately 1 per cent by alpha emission and 99 per cent by orbital electron capture.¹⁷

In the present work qualitative evidence for the presence of Pa^{229} , which was probably formed by the reaction $\text{Pa}^{231}(\text{d}, \text{p}3\text{n})\text{Pa}^{229}$ and by decay of a short-lived K-capturing U^{229} species formed by a $(\text{d}, 4\text{n})$ reaction, was obtained in the following manner. Approximately 20 per cent of the original solution from the first deuteron bombardment was evaporated to dryness and heated under a heat lamp to remove traces of fluoride; the residue was taken up in 6N HNO_3 , and all but 1 per cent of the protactinium and uranium was extracted away by means of diisopropyl ketone. The aqueous layer was made 3N in HF, and 0.3 mg of lanthanum fluoride was precipitated by addition of lanthanum nitrate solution. It was expected that lanthanum fluoride precipitated in this manner would carry actinium but not protactinium. The lanthanum fluoride was washed with a mixture of hydrofluoric and nitric acids, slurried onto large platinum plates, flamed to drive off Fr^{221} , and rapidly placed in an alpha counter to watch for the 5-min growth characteristic of Ac^{225} . However, about 5×10^4 c/min of alpha activity (0.3 per cent of initial alpha activity) was carried on the lanthanum fluoride, and the 5-min growth could not be observed above this background. Then a sample of the lanthanum fluoride precipitate was left for 40 min in an atmospheric alpha counter, and after removal of

the sample the background built up in the counter by recoil atoms was followed and was found to decay with a half life of 47 min. This is believed to indicate Bi^{213} and Po^{213} daughters of Ac^{225} and Pa^{229} .

No evidence for Pa^{229} could be found in alpha-pulse analyses of the protactinium fractions. The limit of detection by this method, assuming 1 per cent alpha branching, gives a cross section of less than $1 \times 10^{-27} \text{ cm}^2$ for formation of Pa^{229} . If there were 5 c/min of K x-rays from Pa^{229} which were unresolved in the beryllium-plus-lead absorption curve of Fig. 3, the cross section for formation of Pa^{229} (assuming 99 per cent decay by K electron capture, one K x-ray per disintegration, and 0.5 per cent counting efficiency) would be $9 \times 10^{-27} \text{ cm}^2$.

An attempt was also made to find Pa^{229} by isolating a protactinium fraction from a portion of the uranium fraction of the first deuteron bombardment 42 hr after the initial separation. The fraction was examined by pulse analysis, and no Pa^{229} was found. This observation is to be expected in view of later work which has shown U^{229} to have a half life of only 58 min.¹⁷

4.4 U^{230} . Alpha-pulse analyses of the uranium fraction soon after separation showed the five peaks characteristic of the U^{230} series,¹³ and the total alpha activity of the uranium fraction decayed with a half life close to the known value for U^{230} , 20.8 days (reference 13). The relative amounts of U^{230} and Pa^{231} were determined by alpha counting of the separated uranium and protactinium fractions and also by alpha-pulse analysis of the original solution of the target material. The yield of U^{230} was greater than could be accounted for by beta decay of Pa^{230} , and the excess corresponded to a cross section of $5 \times 10^{-27} \text{ cm}^2$ for the reaction $\text{Pa}^{231}(\text{d},3\text{n})\text{U}^{230}$ in the first deuteron bombardment and 17×10^{-27} in the second bombardment.

4.5 U^{232} . This isotope was determined quantitatively in two ways: by alpha-pulse analyses of the uranium fraction after the U^{230} series had decayed and by isolating its daughter Th^{228} from the uranium fraction. In the pulse analyses U^{232} was not resolved from Po^{210} and Th^{228} , but the Po^{210} activity could be calculated from the amount of U^{230} originally present in the sample, and the ratio of $\text{Th}^{228}/\text{U}^{232}$ activities could be calculated from the known half lives of Th^{228} (1.90 years, reference 18) and of U^{232} (70 years, reference 19). The Th^{228} content of the thorium isolated from the uranium fraction was determined both by following the growth of alpha activity and by pulse analyses. The chemical yield was measured by means of UX_1 (Th^{234}) tracer.

The yields of U^{232} seemed to be in excess of the amounts arising from the decay of Pa^{232} . From the difference the cross section for the formation of U^{232} by the reaction $\text{Pa}^{231}(\text{d},\text{n})$ was calculated to be

$5 \times 10^{-27} \text{ cm}^2$ in the first deuteron bombardment and $23 \times 10^{-27} \text{ cm}^2$ in the second bombardment. This cross section is very inaccurate because most of the U^{232} came from decay of Pa^{232} and the determination of the Pa^{232} was subject to the usual errors of absolute beta counting.

4.6 U^{231} . A new 4.2-day x-ray activity was found in the uranium fraction and has been tentatively assigned to K electron capture by U^{231} . The assignment has the following basis. From energy considerations the only uranium isotopes which could be produced by bombardment of Pa^{231} with 21-Mev deuterons are U^{232} , U^{231} , U^{230} , and U^{229} , either directly by (d,xn) reactions or from beta decay of protactinium isotopes formed by (d,pxn) reactions. U^{232} and U^{230} had previously been definitely assigned to other activities by identification of daughter activities known in the natural radioactive series.^{13,20} Orbital electron capture by U^{229} was ruled out by the failure to find Pa^{229} by alpha-pulse analysis of a protactinium fraction isolated from the uranium fraction 42 hr after the initial separation, as mentioned in Sec. 4.3. Furthermore, subsequent work by Meinke, Ghiorso, and Seaborg¹⁷ has shown that U^{229} is a 1-hr K-capturing isotope. The possibility that the activity is an isomeric transition seems to be eliminated by the high yield, which is comparable with the yield of U^{230} by the (d,3n) reaction. The remaining possibility is U^{231} .

The half life was determined by observation of the decay of the activity, as shown in Fig. 11. The half life of the long-lived tail due to U^{230} was taken as 20.8 days (reference 13), and a calculated correction for the growth of daughters of U^{230} and U^{232} was applied to the decay curve obtained through thin cellophane. [Cellophane was used to cover the samples of the uranium fraction to avoid contamination of the counter with recoil atoms from the U^{230} series.] The average value of the half life from all the curves is 4.2 ± 0.1 days.

Lead and aluminum absorption curves of the uranium fraction obtained a few days after separation are given in Figs. 12 and 13, respectively. The lead curve has a small component with 3.0 to 3.5 g/cm² half thickness (0.40 to 0.43 Mev); a component with a half thickness of about 210 mg/cm² (70 or 123 Kev), believed to be mainly K x-rays which have an energy of about 100 Kev; and softer components. The aluminum curves show a component with a 5.2 g/cm² half thickness (170 Kev), believed to be mainly K x-rays, and softer components with half thicknesses of 192 mg/cm² (20 Kev) or less. A lead absorption curve with 2.0 g/cm² of beryllium covering the sample was also obtained, and a component with a half thickness of 202 mg/cm² of lead (69 or 121 Kev) and softer components were found. The softer components may not be significant because the decay curves

show that approximately 25 per cent of the activity through cellophane was due to the 20.8-day tail at the time the aluminum absorption curve was determined. Because of the growth of daughters of U^{230} and U^{232} it was not possible to determine the correction by remeasuring the absorption curves after the U^{231} had decayed. The contribution of the 20.8-day tail was not so important for the harder components but may account for the somewhat high values found for the K x-ray energy.

The yield of U^{231} was calculated from the average abundance of the K x-rays in the absorption curves, assuming a counting efficiency of 0.5 per cent and one K x-ray per disintegration. The cross section for the reaction $Pa^{231}(d,2n)U^{231}$ was $3 \times 10^{-27} \text{ cm}^2$ in the first bombardment and $7 \times 10^{-27} \text{ cm}^2$ in the second bombardment.

In order to determine the U^{231} alpha branching and half life for alpha emission, thorium daughters were isolated four times from a portion of the uranium fraction, at times from 42 to 475 hr after the initial uranium separation. The thorium daughters, Th^{227} and Th^{228} , were determined by following the growth and decay of alpha activity in the thorium fraction; Th^{228} was found in all the extractions; Th^{227} was found in the first isolation, but none was found in subsequent thorium extractions. The Th^{227} found in the first thorium extraction probably was a daughter of Pa^{231} and was extracted in small amount with the uranium fraction. From the limit of detection of Th^{227} in these experiments the U^{231} alpha branching is less than 0.05 per cent, and the U^{231} half life is greater than 20 years.

A summary of the reactions and cross sections which were observed in the deuteron bombardments is given in Table 2.

5. RESULTS OF HELIUM-ION BOMBARDMENTS

5.1 Pa^{230} . The only activity found in the protactinium fraction other than Pa^{231} was Pa^{230} . However, the portion of the Geiger-Mueller activity due to the Pa^{230} was too small for absorption curves of this fraction to be useful for characterization of the radiations of Pa^{230} . The yield of Pa^{230} was obtained by chemical isolation of uranium from the protactinium fraction 21 days after the original separation from uranium, using a value of 10 for the K electron/beta branching ratio¹⁴ in the calculations. Pulse analyses showed only U^{230} series in this uranium fraction. From the yield of Pa^{230} a cross section of $6 \times 10^{-27} \text{ cm}^2$ was calculated for the reaction $Pa^{231}(\alpha,n)Pa^{230}$. Some Pa^{230} could conceivably arise from alpha branching of Np^{234} , but, since the upper limit of the alpha branching of Np^{234} is less than 0.1 per cent²¹ (correcting for the K branching of Pa^{230} , reference 14)

and since the observed yield of Np^{234} was smaller than the Pa^{230} yield, it follows that the quantity of Pa^{230} which could have been formed by alpha decay of Np^{234} was entirely negligible.

5.2 U^{230} . The most abundant alpha activity in the uranium fraction, as shown by pulse analyses and also by alpha decay, was the U^{230} series. The yield from all reactions corresponded to a cross section of $0.16 \times 10^{-27} \text{ cm}^2$. All this could be accounted for by beta decay of Pa^{230} , but because of experimental uncertainties the cross section for the formation by the reactions $\text{Pa}^{231}(\alpha, p4n)\text{U}^{230}$ and $\text{Pa}^{231}(\alpha, \alpha n)\text{Np}^{230} \xrightarrow{\text{K}^?} \text{U}^{230}$ might possibly be as large as $0.01 \times 10^{-27} \text{ cm}^2$.

5.3 U^{232} . After decay of the U^{230} series, pulse analyses showed that there was U^{232} in the uranium fraction, and the amount gave a cross section of approximately $9 \times 10^{-27} \text{ cm}^2$ for the reaction $\text{Pa}^{231}(\alpha, p2n)\text{U}^{232}$ plus possibly $\text{Pa}^{231}(\alpha, 3n)\text{Np}^{232} \xrightarrow{\text{K}^?} \text{U}^{232}$.

5.4 U^{229} . About 3 per cent of the initial alpha activity of the uranium fraction seemed to decay with a half life of the order of 1.5 days, corresponding to a cross section of $7 \times 10^{-30} \text{ cm}^2$. In order to determine whether this activity was a real one which could be assigned to U^{229} or merely a spurious instrumental effect, two short helium-ion bombardments were later carried out at the University of California Radiation Laboratory. A combined uranium-neptunium fraction was separated quickly and examined with the pulse analyzer at the Radiation Laboratory. No alpha activities other than the U^{230} series were found, and hence it is believed that the effect was merely instrumental error. Other observers have subsequently produced U^{229} by bombardment of thorium with higher energy helium ions and have shown that it is a 58-min isotope which decays approximately 20 per cent by alpha emission and 50 per cent by capture of an orbital electron.¹⁷

5.5 U^{231} . The 4.2-day x-ray activity which was found in the uranium fractions of the deuteron bombardments was also found in the uranium fraction from the first helium-ion bombardment. Geiger-Mueller decay curves and absorption curves were essentially the same for the uranium fractions from all the bombardments. The total cross section for the formation of U^{231} by the reaction $\text{Pa}^{231}(\alpha, p3n)\text{U}^{231}$ plus possibly the reaction $\text{Pa}^{231}(\alpha, 4n)\text{Np}^{231} \xrightarrow{\text{K}^?} \text{U}^{231}$ was calculated to be $0.4 \times 10^{-27} \text{ cm}^2$ from the abundance of K x-rays found in the absorption curves.

5.6 Np^{234} . An activity with a hard gamma ray (about 1.9 Mev) and K and L x-rays which decayed with a half life of 4.4 days was found in the neptunium fraction. The radiations and half life agree with those found by Hyde, Studier, and Ghiorso²¹ in the neptunium fractions from deuteron and helium-ion bombardments of U^{233} , which have been assigned²¹ to Np^{234} .

Figure 14 shows the decay of the Geiger-Mueller activity in the neptunium fraction through various absorbers, measured on a xenon-filled counter. A 4.2- to 4.4-day component was found in all the decay curves. The best value for the half life was 4.4 days obtained from the decays through 2.0 g/cm² of beryllium and through this amount of beryllium plus 59 mg/cm² of lead.

The yield was determined from the K x-ray component of the absorption curves, assuming a counting efficiency of 0.5 per cent and one K x-ray per disintegration. The cross section for the reaction $\text{Pa}^{231}(\alpha, n)\text{Np}^{234}$ was calculated to be 1.5×10^{-27} cm².

5.7 1.2-Day Neptunium. A neptunium beta activity with a half life of approximately 1.2 days was also found in the decay of Geiger-Mueller activity through cellophane (Fig. 14). The sample was examined for positrons by means of a crude magnet counter, and none were detected. The cross section for the formation of the 1.2-day activity, assuming that it was formed from Pa^{231} , was only 9×10^{-29} cm². The activity is believed to be due to 2.33-day Np^{239} or 2.10-day Np^{238} from a small uranium impurity in the sample of Pa^{231} which was bombarded.

5.8 Alpha Fission Cross Section. A rough value for the cross section for fission of Pa^{231} by 38-Mev helium ions was determined by measuring the yield of Ba^{140} , assuming the same yield curve as for fission of U^{235} by thermal neutrons. A value of 0.3×10^{-24} cm² was obtained.

A summary of the reactions and cross sections observed in the first helium-ion bombardment is given in Table 3.

6. SUMMARY

Bombardments of Pa^{231} have been carried out with 21-Mev deuterons and 42-Mev helium ions. The isotopes produced and identified were Pa^{232} , Pa^{230} , $\text{Pa}^{229}(\text{?})$, U^{232} , U^{231} , and U^{230} in the deuteron bombardments and Pa^{230} , U^{232} , U^{231} , U^{230} , and Np^{234} in the helium-ion bombardments. Cross sections for the various reactions have been determined.

A new uranium isotope with a half life of 4.2 ± 0.1 days, emitting K and L x-rays and a few 0.4-Mev gamma rays, has been found and tentatively assigned to U^{231} . The alpha branching of U^{231} has been found to be less than 0.05 per cent, and the alpha half life is greater than 20 years.

The radiations of Pa^{232} and Np^{234} have been characterized by absorption measurements, and the results were in essential agreement with previous work.

Pa^{230} was found to have a half life of 17.7 ± 0.5 days by observation of the decay of Geiger-Mueller activity through beryllium and lead absorbers, and it was found to have a 0.94-Mev gamma ray, K x-rays, L x-rays, a beta particle with a maximum energy of approximately 430 Kev, and a beta particle with a maximum energy of about 220 Kev. The abundances per beta disintegration into U^{230} , corrected for counting efficiencies and back-scattering, were approximately 5, 9, 14, 0.22, and 1, respectively. These results indicate a K electron/beta branching ratio of 9.

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Table 1—Radiations of Pa^{230} from a Sample with 1.01×10^4 Pa^{230}
Beta Disintegrations per Minute

Radiation	Radiation at no absorber (4.2% geometry), c/min	Back-scattering factor	Counting efficiency	Events/min
220-Kev beta	660	1.60	100	0.98×10^4
430-Kev beta	150	1.60	100	0.22×10^4
L x-rays	114	1.00	2.0	14×10^4
K x-rays	19	1.00	0.5	9.0×10^4
0.94-Mev gamma	21	1.00	1.0	5.0×10^4

Table 2—Reactions and Cross Sections Observed in
Bombardment of Pa^{231} with 21-Mev Deuterons

Reaction	Cross section, cm^2	
	Bombardment 1	Bombardment 2
$\text{Pa}^{231}(\text{d}, \text{p})\text{Pa}^{232}$	40×10^{-27}	60×10^{-27}
$\text{Pa}^{231}(\text{d}, \text{p}2\text{n})\text{Pa}^{230}$	23×10^{-27}	27×10^{-27}
$\text{Pa}^{231}(\text{d}, \text{p}3\text{n})\text{Pa}^{229}$	$<1 \times 10^{-27}$	
+ $\text{Pa}^{231}(\text{d}, 4\text{n})\text{U}^{229} \xrightarrow{\text{K}} \text{Pu}^{229}$		
$\text{Pa}^{231}(\text{d}, \text{n})\text{U}^{232}$	5×10^{-27}	23×10^{-27}
$\text{Pa}^{231}(\text{d}, 2\text{n})\text{U}^{231}$	3×10^{-27}	7×10^{-27}
$\text{Pa}^{231}(\text{d}, 3\text{n})\text{U}^{230}$	5×10^{-27}	17×10^{-27}

Table 3—Reactions and Cross Sections Observed in Bombardment of Pa^{231} with 42-Mev Helium Ions

Reaction	Cross section, 10^{-27} cm^2
$\text{Pa}^{231}(\alpha, \alpha n)\text{Pa}^{230}$	6
$\text{Pa}^{231}(\alpha, p2n)\text{U}^{232}$	9
+ $\text{Pa}^{231}(\alpha, 3n)\text{Np}^{232} \xrightarrow{K?} \text{U}^{232}$	
$\text{Pa}^{231}(\alpha, p3n)\text{U}^{231}$	0.4
+ $\text{Pa}^{231}(\alpha, 4n)\text{Np}^{231} \xrightarrow{K?} \text{U}^{231}$	
$\text{Pa}^{231}(\alpha, p4n)\text{U}^{230}$	<0.01
+ $\text{Pa}^{231}(\alpha, 5n)\text{Np}^{230} \xrightarrow{K?} \text{U}^{230}$	
$\text{Pa}^{231}(\alpha, n)\text{Np}^{234}$	1.5
$\text{Pa}^{231}(\alpha, \text{fission})$	300

					Np^{234} K 4.40 days	Np^{235} K 400 days
		U^{230} α 20.8 days		U^{232} α 70 years	U^{233} α 1.62×10^5 years	U^{234} α 2.35×10^5 years
		Pa^{229} K $\alpha(0.1\%)$ 1.4 days	Pa^{230} β^- 17 days	Pa^{231} α 3.43×10^4 years	Pa^{232} β^- 1.4 days	Pa^{233} β^- 27.4 days
Th^{226} α 30.9 min	Th^{227} α 18.9 days	Th^{228} α 1.90 years	Th^{229} α 7000 years	Th^{230} α 8.3×10^4 years	Th^{231} β^- 24.6 hr	Th^{232} α 1.39×10^{10} years
Ac^{225} α 10.0 days		Ac^{227} $\beta^-(99\%)$ $\alpha(1.2\%)$ 13.5 years	Ac^{228} β^- $\alpha(\text{small } \%)$ 6.13 hr			

Fig. 1—Isotopes in the region of Pa^{231} which were known at the beginning of these bombardments.

Fig. 2—Decay of protactinium fraction from deuteron bombardment, through 2.0 g/cm^2 of beryllium plus 5.1 g/cm^2 of lead. (A) Gross decay curve. (B) Decay curve corrected for Pa^{231} Geiger-Mueller activity. Resolution is shown into a 17.7-day period (Pa^{230}) and a 32-hr period (Pa^{232} , curve C).

Fig. 3—Absorption of Pa^{232} electromagnetic radiations in lead. Sample covered with 2.0 g/cm^2 of beryllium. (A) Total activity. (B) Absorption curve of Pa^{232} , obtained by correcting curve A for Pa^{230} (curve C) and for Pa^{231} (curve D). The half thickness of the Pa^{232} hard gamma ray is 10.1 g/cm^2 of lead (1.02 Mev).

Fig. 4—Absorption of Pa^{232} electromagnetic radiations in lead. Sample covered with 2.0 g/cm^2 of beryllium. (A) Total activity. (B) Absorption curve of Pa^{232} , obtained by correcting curve A for activity due to Pa^{230} (C) and Pa^{231} (D). After subtraction of the Pa^{232} hard gamma ray (E), curve B can be resolved into a gamma ray of 800 mg/cm^2 half thickness (F) and a component with a 11 mg/cm^2 half thickness (G), probably L x-rays.

Fig. 5—Absorption of Pa^{232} radiations in aluminum. (A) Total activity. (B) Pa^{232} aluminum absorption curve, obtained by correcting curve A for Pa^{230} (Figs. 9 and 10, corrected for decay) and for Pa^{231} (C). Resolution of a hard gamma component and of L x-rays (D) with half thickness of 78 mg/cm² (14.6 Kev) is shown.

Fig. 6—Absorption of Pa^{232} radiations in aluminum. (A) Total activity. (B) Pa^{232} aluminum absorption curve, obtained by correcting curve A for Pa^{230} (Figs. 9 and 10, corrected for decay) and for Pa^{231} (Fig. 5, curve C). (E) Curve B less hard gamma and L x-rays (see Fig. 5), showing beta component with a range of about 150 mg/cm² (480 Kev) and initial half thickness of 33 mg/cm², assumed from Jaffey and Van Winkle's results.¹¹ (F) Curve E less beta component with a 33 mg/cm² initial half thickness, showing beta component with a 6.9 mg/cm² initial half thickness and a range of about 70 mg/cm² (about 280 Kev). (G) Soft beta component with an initial half thickness of 1.9 mg/cm² and a range of about 16 mg/cm² (about 90 Kev). The softest component was not observed in Pa^{232} by Jaffey and Van Winkle and may be spurious or due to Pa^{229} .

Fig. 7—Absorption of Pa^{230} electromagnetic radiations in lead. Sample covered with 2.0 g/cm² of beryllium. (A) Total activity. (B) Absorption curve of Pa^{230} , obtained by correcting curve A for Pa^{231} and Pa^{232} (Figs. 3 and 4, corrected for Pa^{232} decay). The gamma component with a half thickness of 9.4 g/cm² (0.94 Mev) is shown.

Fig. 8—Absorption of Pa^{230} electromagnetic radiations in lead. Sample covered with 2.0 g/cm^2 of beryllium. (A) Total activity. (B) Absorption curve of Pa^{230} , obtained by correcting curve A for Pa^{231} and Pa^{232} (Fig. 4, corrected for Pa^{232} decay). (C) 0.94-Mev gamma ray. (D) Curve B less curve C, showing component with a half thickness of 245 mg/cm^2 (74 or 131 Kev), probably K x-rays. (E) Curve D less 245 mg/cm^2 component, showing component with a half thickness of 10.8 mg/cm^2 (23 Kev), probably L x-rays.

Fig. 9—Absorption of Pa^{230} radiations in aluminum. (A) Total activity. (B) Aluminum absorption curve of Pa^{230} , obtained from curve A by correcting for Pa^{231} and Pa^{232} (Figs. 5 and 6, corrected for Pa^{232} decay), showing hard component. (C) Curve B less hard component, showing L x-ray component with a half thickness of 79 mg/cm^2 (14.6 Kev).

Fig. 10—Absorption of Pa^{230} radiations in aluminum. (A) Total activity. (B) Aluminum absorption curve of Pa^{230} , obtained from curve A by correcting for Pa^{231} and Pa^{232} (Figs. 5 and 6, corrected for Pa^{232} decay). (D) Curve B less hard gamma ray and L x-rays (Fig. 9). This is resolved into beta components with ranges of about 130 mg/cm² (430 Kev), 50 mg/cm² (220 Kev, curve E), and 13 mg/cm² (80 Kev).

Fig. 11 — Decay of Geiger-Mueller activity in uranium fraction from first deuteron bombardment. (A) Through cellophane (12.1 mg/cm² total absorber). (B) Curve A less calculated correction for growth of daughters of U²³⁰ and U²³². (C) Through 2.0 g/cm² of beryllium. (D) Through 2.0 g/cm² of beryllium plus 77 mg/cm² of lead. The curves are resolved into 20.8-day and 4.1- to 4.4-day half lives.

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Fig. 12—Lead absorption curves of uranium fraction, resolved into curve A, 3.5 g/cm² half thickness (0.43 Mev); curve B, 210 mg/cm² half thickness (7C or 123 Kev); curve C, 46 mg/cm² half thickness (40 Kev); and curve D, 10 mg/cm² half thickness (13 or 22 Kev).

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Fig. 13—Aluminum absorption curves of uranium fraction, resolved into curve A, 5.2 g/cm² half thickness (170 Kev); curve B, 192 mg/cm² half thickness (20 Kev); and curve C, 45 mg/cm² half thickness (13.5 Kev).

Fig. 14—Decay of Geiger-Mueller activity in neptunium fraction from helium-ion bombardment. (A) Decay through cellophane. (B) Half life, 4.2 days; curve A less long-lived tail (C) due to Pa^{231} contaminant. (D) Approximately 1.2-day component of decay through cellophane. (E) Half life, 4.4 days; decay through 2.0 g/cm^2 of beryllium. (F) Half life, 4.4 days; decay through 2.0 g/cm^2 of beryllium plus 59 mg/cm^2 of lead. (G) Half life, 4.4 days; decay through 5.0 g/cm^2 of lead. Obtained on xenon-filled counter.

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Paper 9.10

THERMAL-NEUTRON FISSION PROPERTIES OF Th^{228} (RdTh)

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ABSTRACT

An upper limit of $0.3 \times 10^{-24} \text{ cm}^2$ has been set for the cross section of Th^{228} (RdTh) for fission with thermal neutrons.

Recent improvements in the design of fission counters¹ have made possible the determination of fission cross sections with very small samples by utilizing the high neutron intensities available in uranium chain-reacting piles. With this technique, using the thermal column of the Argonne heavy-water pile, an upper limit of $0.3 \times 10^{-24} \text{ cm}^2$ has been set for the fission cross section of 1.9-year Th^{228} (RdTh) with thermal (cadmium-absorbable) neutrons.

The Th^{228} was isolated from an old Ra^{228} (MsThI) solution by an extraction procedure which separated it from parent and daughter activities as well as from possible plutonium or uranium contamination. The reagent was a 0.15M solution of α -thenoyl trifluoroacetone (TTA) in benzene, a reagent which is specific for quadrivalent ions under the conditions of the extraction.² The aqueous MsTh solution was 0.5M in hydrochloric acid, 0.1M in hydrazine, and 0.1M in ammonium iodide. The hydrazine and ammonium iodide were present to reduce any plutonium which may have been present to a nonextractable trivalent state.³ The aqueous solution was extracted with three times its volume of organic phase, and the organic layer was washed with a solution 0.5M in hydrochloric acid, 0.1M in hydrazine, and 0.1M in ammonium iodide. The Th^{228} was extracted from the organic phase into 5.0M

hydrochloric acid, and this solution was used as a stock solution for samples used in the fission measurements.

The first measurements were made on a sample which contained 4.46×10^7 dis/min (2.44×10^{-8} g) of Th^{228} . A fission rate of 200 fissions per minute was observed over a background of 100 fissions per minute. The neutron flux was determined by measuring the rate of fission of a known weight of U^{235} which has a fission cross section of $521 \times 10^{-24} \text{ cm}^2$ under the same conditions.⁴ The flux was found to be 4.8×10^{12} neutrons/min/cm². The cross section is then given by the equation

$$\sigma(\text{fiss}) = \frac{R}{FN}$$

where R = observed fission rate

F = neutron flux per square centimeter

N = total number of atoms in the sample

$\sigma(\text{fiss})$ = fission cross section of the isotope being measured

A value of $0.63 \times 10^{-24} \text{ cm}^2$ was calculated for the fission cross section of Th^{228} .

Another sample of the stock solution of Th^{228} was put through two more cycles of purification as described above. A sample which contained 5.2×10^7 dis/min (2.84×10^{-8} g) of Th^{228} showed a fission rate of 93 fissions per minute at a flux of 4.9×10^{12} neutrons/min/cm². This corresponds to a fission cross section of $0.25 \times 10^{-24} \text{ cm}^2$.

It is apparent that some fissionable contaminant was present in the first sample which was materially reduced in the additional purification of the second sample. Since it is not known whether the fissionable impurity was completely removed, it is only possible to set an upper limit for the fission cross section. Upon consideration of the possible errors in the experiment it is probably safe to say that an upper limit for the fission cross section of Th^{228} is $0.3 \times 10^{-24} \text{ cm}^2$.

ACKNOWLEDGMENTS

The authors are pleased to acknowledge the cooperation of W. H. Zinn in making available the facilities of the Argonne heavy-water pile and their indebtedness to G. T. Seaborg and W. M. Manning under whose general direction the experiments were performed.

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Paper 9.11

THERMAL-NEUTRON FISSION PROPERTIES OF U^{232}

By. Q. Van Winkle, R. Elson, W. C. Bentley, and Albert Ghiorso

[Editor's Note: Contribution from the Argonne National Laboratory. Based on Report CF-3798. Prepared for publication Apr. 1, 1947.]

ABSTRACT

The thermal-neutron fission cross section of U^{232} has been determined to be $83 \pm 15 \times 10^{-24}$ cm².

Two samples of U^{232} have been prepared by neutron irradiation of Pa^{231} according to the reaction

The first of these irradiations was performed in the Argonne heavy-water pile on a 0.23-mg sample of Pa^{231} . A bombardment of approximately 7500-kwh resulted, after chemical separation, in a U^{232} sample containing 58,500 alpha c/min (52 per cent counting yield) which, assuming a U^{232} half life of 70 years,¹ corresponds to a weight of 2.30×10^{-9} g. The second bombardment was performed in the Clinton pile and resulted in the isolation, from 1.23 mg of Pa^{231} , of 8.11×10^6 alpha c/min of U^{232} (0.319×10^{-6} g).

The chemical procedures employed in separating a uranium fraction from the protactinium included the following operations. The irradiated protactinium oxide was dissolved in hydrofluoric acid, and the resulting solution was evaporated to dryness in a platinum dish. The residue was dissolved in a small volume of 2N nitric acid. (The solubility of the protactinium was enhanced by the presence of a trace of fluoride remaining after evaporation.) This solution was made 10N in

ammonium nitrate, adjusted to 1N nitric acid, and equilibrated against two volumes of diethyl ether. The ether equilibration was repeated four times with fresh portions of ether. Each ether layer was washed twice with 0.1N nitric acid-10N ammonium nitrate solution. Finally the U^{232} was removed from the washed ether layers by equilibration against an equal volume of pure water. This final water layer was evaporated to dryness, and the residue was dissolved in a small amount of 1N nitric acid. In the case of the Argonne bombardment, this solution was delivered onto a platinum plate of 1 in. diameter and 2 mil thickness and evaporated under a heat lamp. The U^{232} obtained from the Clinton bombardment was electrodeposited in a thin uniform layer on platinum foil by Britain.²

Fission measurements were made in the thermal column of the Argonne heavy-water pile using the high-sensitivity fission-counting apparatus described by Ghiorso and Bentley.³ The 2.30×10^{-9} g sample of U^{232} gave a fission rate of 290 fissions per minute over a background of 125 fissions per minute. Under identical conditions of neutron flux a standard thin sample of Pu^{239} showed a rate of 1130 fissions per minute per 10^{-9} g. Assuming that all the fissions observed from the U^{232} sample were due to U^{232} and using a value of 765×10^{-24} cm² (reference 4) for the thermal-neutron fission cross section of Pu^{239} , the thermal-neutron fission cross section of U^{232} is

$$\sigma(\text{fiss}) = \frac{290 \times 232}{2.3} \times \frac{1}{1130 \times 239} \times 765 \times 10^{-24} = 83 \times 10^{-24} \text{ cm}^2$$

A fission rate of 40,100 fissions per minute was observed for the second (0.319×10^{-6} g) sample of U^{232} under conditions such that the fission rate of the Pu^{239} standard was 1115 fissions per minute per 10^{-9} g. The thermal-neutron cross section calculated for U^{232} from this measurement is

$$\sigma(\text{fiss}) = \frac{40,100 \times 232}{319} \times \frac{1}{1124 \times 239} \times 765 \times 10^{-24} = 83 \times 10^{-24} \text{ cm}^2$$

The thermal nature of the neutrons employed was confirmed by repeating the measurements with the fission chamber surrounded by a cadmium shield 0.027 in. thick. Under these conditions fission rates were reduced by a factor of 100 or more.

The possibility that the fission found is due to an appreciable amount of natural uranium impurity in the original bombarded Pa^{231} is eliminated by the fact that, using starting material of the same purity, concordant results were obtained from bombardments of wide-

ly differing neutron intensity. It would appear that the chief uncertainty in the absolute thermal-neutron fission cross section of U^{232} lies in the value of its half life (70 ± 10 yr).¹ In view of this circumstance the cross section is given as $83 \pm 15 \times 10^{-24}$ cm².

ACKNOWLEDGMENTS

The authors are pleased to acknowledge the cooperation of W. H. Zinn in making available the facilities of the Argonne heavy-water pile and their indebtedness to G. T. Seaborg and W. M. Manning under whose general direction the experiments were performed. Thanks are also due the staff of Oak Ridge National Laboratory, Oak Ridge, Tenn., who handled the neutron bombardment of the Pa^{231} sample.

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Paper 9.12

THERMAL-NEUTRON FISSION PROPERTIES
OF Pa^{231} , Th^{232} , AND Th^{230}

By Albert Ghiorso and Q. Van Winkle

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1949.]

ABSTRACT

Pa^{231} , Th^{232} , and Th^{230} have been measured for thermal-neutron (i.e., cadmium-absorbable) fissionability by means of the high-sensitivity fission-pulse measuring method. Pa^{231} has a definite thermal cross section of

0.010 ± 0.005 barn; Th^{232} , not greater than 2×10^{-5} barn; and Th^{230} , not greater than 0.001 barn.

1. Pa^{231}

Several samples of Pa^{231} were tested for thermal-neutron fissionability at a time when the sensitivity and reliability of the fission ion-chamber apparatus were not very great. Values between 0.008 and 0.04 barn were obtained with sample plates which at times were quite thick.

A more recent measurement made use of the Pa^{231} which was used in making U^{232} in the Clinton pile. After the U^{232} had been completely removed a thin plate containing 170 μg of Pa^{231} was prepared and counted. There were 4270 fissions per minute at a sensitivity such that

$$\sigma(\text{fiss}) \text{ barns} = 414 \times \frac{\text{fissions per minute}}{\mu\mu\text{g of Pa}^{231}}$$

$$\sigma = 414 \times \frac{4270}{170 \times 10^6} = 0.010 \text{ barn}$$

2. Th^{232}

Only one determination of the fissionability of Th^{232} was made. One sample of about 500 μg was prepared from material whose past chemical history, and thus its purity, was known. At a neutron flux such that the sensitivity factor was 622, this sample had a net fission rate of 55 fissions per minute with a cadmium shield over the chamber and 73 fissions per minute without the shield in place. The difference of about 20 fissions per minute due to thermal neutrons would correspond then to an upper limit for the fission cross section for Th^{232} of

$$\sigma(\text{fiss}) = 622 \times \frac{20}{500 \times 10^6} = 2 \times 10^{-5} \text{ barn}$$

3. Th^{230}

Only one fissionability determination was made for Th^{230} . This isotope as it occurs in nature is mixed with several times as much Th^{232} . The sample used for measurement consisted of about 100 μg of Th^{230} and 350 μg of Th^{232} . At the same sensitivity used for the Th^{232} measurements the fission rate without cadmium filtering was 258 fissions per minute, and with cadmium the rate was 71 fissions per minute. By correcting for the effect due to Th^{232} alone by using the preceding data on that isotope, it can be seen that the thermal-neutron fission rate due to Th^{230} is equal to or less than about 200 fissions per minute. Its cross section then must not be greater than 0.001 barn.

Paper 9.13

COUNTING EFFICIENCY OF A MICA-WINDOW GEIGER-MUELLER TUBE FOR 0.3-MEV GAMMA RAYS

By Martin H. Studier

[Editor's Note: Contribution from the Argonne National Laboratory.
Based on Report CP-3642. Prepared for publication Sept. 5, 1946.]

ABSTRACT

The counting efficiency of a brass-walled mica-window argon-filled Geiger-Mueller tube has been measured for 0.3-Mev gamma rays and found to be approximately 0.5 per cent.

1. INTRODUCTION

The absolute measurement of gamma rays with a Geiger-Mueller counter is complicated by the fact that the counting efficiency [throughout this paper "counting efficiency" is defined as the probability of recording a ray which passes through the sensitive region of a counter] for electromagnetic radiation is a function of the type of tube. Although the counting efficiency for particle radiation is essentially 100 per cent, it is much lower for quantum radiation because of the low specific ionization of electromagnetic radiation. For quantum energies above 0.1 Mev, absorption in the gas of a Geiger-Mueller tube is negligible, and gamma rays are counted principally as the result of emission of secondary electrons from the walls of the tube.¹ The counting efficiency is then the probability that an electron will be ejected from the walls into the sensitive region of the tube. It is a function of quantum energy, atomic number of the wall material, and the angle with which the rays strike the walls.

It has been reported that the counting efficiency of tubes made of brass or other light material is very nearly proportional to gamma-ray energy from 0.1 to 3.0 Mev.^{1,2} Presumably it is then necessary to determine only one point to get a complete calibration curve for the counting efficiency in this range. The Geiger-Mueller tubes which have been used on the Plutonium Project for both routine analysis and research are predominantly of one type.³ It was therefore of interest to determine the gamma-ray counting efficiency of such a tube.

2. EXPERIMENTAL WORK

The tube mentioned above consists of a cylinder of $\frac{1}{16}$ -in. brass, $2\frac{1}{2}$ in. long and $1\frac{1}{8}$ in. in diameter. The cylinder is covered at one end by a thin-mica window and at the other end by a glass bell with a central capillary through which is sealed a piece of 0.008-in. tungsten wire with a bead of glass fused over the end near the mica window. The tube is filled to a pressure of 10 cm Hg with a mixture of 10 per cent ethanol and 90 per cent argon.

In order to determine the counting efficiency for gamma rays, a source with a known gamma disintegration rate is required. Pa^{231} , the long-lived alpha emitter from the actinium series, was used as a gamma-ray source. This isotope was chosen because its gamma disintegration rate can be determined directly from its alpha disintegration rate. It has been shown that the alpha-ray spectrum of Pa^{231} consists of two distinct groups differing in energy by approximately 0.3 Mev, with the lower energy group comprising 13 per cent of the total.^{4,5} From magnetic deflection experiments, Meitner⁶ obtained the conversion-electron spectrum and deduced that two gamma rays are present with energies of 0.293 and 0.323 Mev, respectively. This makes it probable that one gamma ray of 0.3-Mev energy is emitted by each nucleus formed through emission of a low-energy alpha particle to bring it to the ground state.

A lead absorption curve was obtained on a sample of freshly purified Pa^{231} having an alpha disintegration rate of 2.9×10^6 dis/min. The Geiger-Mueller tube described above was wrapped with $\frac{1}{2}$ in. of lead, and the absorbers were placed directly over the mica window to minimize the effect of scattered radiation.⁷ The sample, mounted on quartz, was placed 1.8 cm from the window of the tube. From the tube and sample dimensions and from the distance of the sample from the window, it was calculated that the sensitive portion of the counting tube would intercept 10 per cent of the gamma radiation emitted by the sample.

The lead absorption curve (see Fig. 1) showed the presence of a single component with a mass-absorption coefficient μ/ρ of 0.394 in the range from 0.25 to 9.5 g/cm² of lead. By using the data of Jones⁸ an energy of 0.308 Mev was deduced for the gamma ray. This represents an average of the energy of the two gamma rays reported by Meitner since the resolution obtained by the absorption method is not very great. By extrapolation to zero absorber a counting rate of 170 c/min was obtained for the 0.3-Mev ray. Using the calculated geometry factor of 10 per cent and 13 per cent of the alpha disintegration for the gamma disintegration rate, the counting efficiency was calculated to be

$$E = \frac{170 \times 10}{2.9 \times 10^6 \times 0.13} = 0.0045$$

This represents a minimum value for the counting efficiency for a 0.3-Mev gamma ray because no correction has been made for the internal conversion of the gamma ray. Absorption curves with aluminum and beryllium showed the presence of 0.2-Mev conversion electrons, and from their abundance it was calculated that the degree of conversion of the 0.3-Mev gamma ray is approximately 15 per cent. Upon applying this correction for internal conversion, the counting efficiency for a 0.3-Mev gamma ray is calculated to be 0.5 per cent.

ACKNOWLEDGMENTS

Pure samples of Pa²³¹ were furnished by D. W. Osborne and R. G. Larson. Acknowledgment is made of the suggestion of the investigation by L. I. Katzin and his critical interest in its progress.

Fig. 1 — Lead absorption curve of radiation from Pa^{231} .

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Paper 9.14

GAMMA-RAY EMISSION BY U^{235}

By Benjamin F. Scott

[Editor's Note: Contribution from the Argonne National Laboratory. Based on Report CC-3715. Prepared for publication Nov. 20, 1946.]

ABSTRACT

The emission of a gamma ray of 187-Kev energy by U^{235} is confirmed through comparison of the absorption in lead of the radiation from two specimens of enriched uranium. The gamma-to-alpha ratio obtained is 0.7, in agreement with the values suggested by experiments of others.

1. INTRODUCTION

A recent measurement of the ratio of the activity of U^{235} to half the combined activities of U^{238} and U^{234} in normal uranium has been reported by Clark, Spencer-Palmer, and Woodward.¹ The half life for alpha emission of U^{235} could be computed from their direct measurement of this ratio. They used an alpha pulse analyzer and reported for $A_{U^{235}} / [(A_{U^{238}} + A_{U^{234}}) / 2]$ a value of 0.0363 ± 0.0003 , which was 21.3 per cent lower than the value 0.0460 determined indirectly by Nier² on the basis of analysis of the radiogenic lead isotopes from several minerals. It was also lower than the value given by Francis and Tcheng³ computed by determining the protactinium-to-uranium ratios in several minerals. This value, when corrected for more recent energy measurements and activity and abundance ratios, is 0.0429.

A possible explanation of the disagreement of the directly measured ratio with the indirectly measured one is the existence of fine structure in the alpha emission spectrum from U^{235} . A group of long-range alpha rays from U^{235} might be masked by the activity from U^{234} and

hence be undetected by a pulse analyzer. The existence of a short-range group masked by the U^{238} activity is not likely because experiments by the British workers showed that in uranium enriched in U^{235} the activity ratio U^{235}/U^{238} was in agreement with the isotope ratio as determined by the mass spectrograph. This explanation demands that gamma radiation accompany approximately 80 per cent of the alpha disintegrations of U^{235} .

Information concerning the existence of a gamma ray from U^{235} was reported by Studier,⁴ who found a 170-Kev gamma component in lead absorption curves of uranium enriched to 82.5 per cent U^{235} . This component was not observed in a thorium fraction isolated from this material or in normal uranium. Macklin⁵ also observed gamma radiation in uranium compounds that persisted after chemical purification and whose abundance seemed to correlate roughly with the known U^{235} content of the various specimens with which he was working. The experiments reported here substantiate the existence of gamma radiation of 187-Kev energy from U^{235} .

2. EXPERIMENTAL WORK

The absorption curves in Figs. 1 to 3 compare the absorption in lead of the radiation from two specimens of enriched uranium found by mass-spectrographic analysis to contain 97.0 per cent and 65.3 per cent of U^{235} , respectively. Gamma radiation with a half thickness in lead of 550 mg/cm² is shown to be emitted by a sample before and after extraction with ethyl ether, indicating that the radiation is due to uranium itself and not to decay products (Fig. 1). A comparison of alpha and gamma emissions shows that there is one alpha particle emitted by U^{235} for every 0.7 gamma quanta at zero absorber, if Nier's ratio is assumed. This value of 0.7 is of course uncertain owing to the effects of scattering on the slope of the absorption curve and the uncertainties in the counting efficiency and solid-angle geometry assumed. In view of this uncertainty the ratio is in good agreement with the value expected from the pulse-analysis data cited above.

The curves of Fig. 2 indicate that the gamma activity correlates closely with the amount of U^{235} present. Figure 3, an absorption curve of the 65.3 per cent material after extraction with ethyl ether, shows that no harder radiation is detectable from 1.5 g or less of U^{235} . Thus it seems that there is little likelihood of another large group of U^{235} alphas. From these data the conclusion may be drawn that U^{235} emits alpha particles of 4.40 Mev (70 per cent) and approximately 4.59 Mev (30 per cent).

Fig. 1—Lead absorption curve, 97 per cent U^{235} , before and after ether extraction.

Fig. 2—Comparison of the absorption in lead of the radiation from 97 per cent U^{235} and 65.3 per cent U^{235} in pyrex tubes.

Fig. 3—Lead absorption curve, 65.3 per cent U^{235} , after ether extraction.

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Paper 9.16

THERMAL-NEUTRON CAPTURE CROSS SECTION OF Pa^{231}

By A. H. Jaffey and Q. Van Winkle

[Editor's Note: Contribution from the Argonne National Laboratory. Based on Report ANL-4283. Preliminary calculations on the work reported here were presented in Chemical Research—Basic Chemistry of Pu, report for month of May 1945, Report CN-3001. Paper written by A. H. Jaffey. Prepared for publication May 9, 1949.]

ABSTRACT

By beta-ray measurement of the Pa^{232} formed in the neutron bombardment of Pa^{231} , the average "effective" thermal-neutron capture cross section of Pa^{231} in the thimble of the Chicago heavy-water pile was found to be about 180 barns.

1. INTRODUCTION

Pa^{231} plays somewhat the same role in piles producing U^{233} from Th^{232} as does Np^{237} in piles producing Pu^{239} from U^{238} . A closely analogous chain of decays and reactions exist starting with U^{238} and Th^{232} , the analogy going so far as to result in closely similar half lives. The following reactions

are similar to the analogous reactions

From the known yield of U^{237} in the heterogeneous graphite pile and from the $\text{Np}^{237}(n,\gamma)$ cross section, it is possible to calculate the Pu^{238} yield.²² Such calculations show that the reactions (1b) are sufficient to account for all the Pu^{238} found associated with the Pu^{239} .

It was felt desirable to determine whether the cross section of Pa^{231} would turn out to be as large as that of Np^{237} , thus completing the analogy.

The experiment reported here involved a measurement of the Pa^{231} effective thermal-neutron capture cross section (see Sec. 3.1 for a more complete definition of this term). The measurements were of a fairly crude nature, and it was hoped at the time that they could be refined into more accurate results. However, up to the time of writing, no really accurate measurement has been made, and the preliminary work is reported here despite its known lack of accuracy.

The activation cross section of a nuclide B [nuclide is defined as "a species of atom characterized by the constitution of its nucleus, in particular by the numbers of protons and neutrons in its nucleus"²¹] may be defined by the equation

$$N_A = N_B \sigma_B nvt \quad (3)$$

where N_A = number of new nuclei formed from B in time t

N_B = number of nuclei of B

nv = average neutron flux (see Sec. 3.1), neutrons/sec/cm²

σ_B = activation cross section of B, cm²

The quantities subject to the greatest errors in the cross-section measurement were N_A and nv . These uncertainties set the limit on the accuracy of the (n,γ) cross-section measurement.

2. MEASUREMENTS

2.1 Method. A Pa^{231} sample was bombarded in the thimble at the center of the Argonne heavy-water pile for about one-half day; the thermal neutron flux was evaluated with a gold-foil monitor placed next to the sample. The amount of Pa^{232} formed was determined by counting its beta radiations with a Geiger-Mueller counter.

2.2 Chemical Operations. Twelve micrograms of Pa^{231} was precipitated in a quartz tube with ammonia, washed with water and methanol, dried at 100°C , and sealed in the tube for bombardment in the Argonne pile thimble. After bombardment, the material was slurried out of the quartz tube with 8N HNO_3 and transferred to a small platinum dish, in which the slurry was evaporated to dryness under a heat lamp. Concentrated HF was added, and the resulting solution was again evaporated to dryness under a heat lamp; this treatment converted the Pa^{231} to a soluble form. The dried residue was dissolved in 8N HNO_3 , and the solution was transferred to a calibrated volumetric flask. Samples were prepared by taking aliquots and evaporating them on glass plates.

Some time after this experiment, the amount of Pa^{231} in these aliquots was determined by solution from the plate and separation from the daughter activities grown in. Pa^{233} (27.4-day beta emitter) tracer was added to two plates and all activity (beta and alpha) was removed with concentrated H_2SO_4 and HF . The solution was fumed with added HF and H_2SO_4 to complete exchange between the Pa^{231} and the Pa^{233} tracer. The HF was removed, and the entire solution was evaporated to dryness, after which the Pa was dissolved in concentrated HCl and extracted with diisopropyl ketone. The activity was separated from the ketone, mounted on a plate, and counted. The Pa^{233} yield gave a measure of the chemical yield (75 per cent).

2.3 Measurement of the Pa^{232} Formed. The beta activity of the Pa^{232} on the glass plates was measured with two mica-window Geiger-Mueller tubes, and the decay was followed for about five half lives. The half-life value determined from this experiment and other work was reported elsewhere,² giving a result of 1.32 days. The decay of five samples was followed until the residual activity (due to Pa^{231}) leveled off and showed no further decay. The constant activity was subtracted, and the Pa^{232} activity was extrapolated to zero time (end of bombardment). All counts were corrected for coincidence of counts (resolution losses). On tube 1 (window thickness 2.77 mg/cm^2), the average of the extrapolated activity was $71,800 \pm 2000 \text{ c/min}$ (average deviation); on tube 2 (3.59 mg/cm^2), it was $63,000 \pm 1250 \text{ c/min}$.

To determine the Pa^{232} disintegration rate from the zero-time counting rates, it was necessary to correct for (1) contributions to the counting rate by radiations other than beta particles, (2) extrapolation to zero absorber, window and air absorption, (3) geometry (assuming isotropic beta-particle emission), and (4) back-scattering from the "infinitely thick" glass mount.

To determine the fraction of the recorded activity due to Pa^{232} beta particles, absorption curves were determined, and an attempt was made to unravel the decay scheme. These measurements have been

reported elsewhere.³ It was not possible to determine the decay scheme from the absorption curves obtained, and as yet the decay scheme is not accurately known. An analysis of the absorption curves showed a number of components, the most abundant of which was apparently a beta particle with an initial half thickness of 5.8 mg/cm^2 (approximately 280 Kev). A relatively small part of the counts in the Geiger-Mueller tube was due to other components, which included L x-rays and a hard gamma ray; the 5.8 mg/cm^2 component accounted for 90.0 per cent of the counts. The assumption that this component is due solely to a beta particle and that the other components are not was made in order to calculate the correction due to other radiations. While this assumption could not be confirmed without a complete decay-scheme analysis, it was probably the most reasonable one that could be made with the data available.

The zero-absorber extrapolation was calculated by using the 5.8 mg/cm^2 half-thickness value for the beta-particle radiation and total absorber values (window plus air) of 3.08 mg/cm^2 for tube 1 and 3.90 mg/cm^2 for tube 2.

The geometry of the first shelf was calibrated by the use of two secondary UX standards loaned by D. W. Engelkemeir. These were made of uranium oxide and had been calibrated against practically weightless samples of UX precipitated from known amounts of "old" uranium and mounted on very thin mica (to reduce back-scattering).^{4,5} Tube 1 was found to have a geometry of 26.0 per cent (average of 26.5 per cent from one standard and 25.4 per cent from the other), while tube 2 had a geometry of 24.0 per cent (average of 23.8 and 24.2 per cent).

The problem of evaluating the increase in counting rate due to back-scattering is difficult in the case of radiation as soft as that of Pa^{232} . Experimental values are available for the increase in counting rate of samples when mounted on various materials.⁶⁻⁸ For samples mounted on glass, the correction factor for radiation of 0.2 to 0.3 Mev is 1.13. However, this factor simply represents the increase in counting rate over that occurring with the sample on an infinitely thin mount and does not necessarily give the increase in the extrapolated zero-absorber rate. Since back-scattered radiation is degraded in energy, the initial part of the absorption curve for the back-scattered fraction should be steeper than that of the primary radiation, as should be the absorption curve for the combined radiations. Since the back-scattered radiation of soft betas would be preferentially absorbed in the mica window and air, it would be expected that the back-scattering correction at the zero-absorber extrapolation would be larger than the value 1.13. On the basis of this reasoning, Jaffey and

Magnusson¹⁰ calculated a back-scattering correction of 1.28 for 0.2-Mev beta radiation in Np^{238} . However, the Np^{238} disintegration rate calculated was too low by 13 per cent since it gave too low a value for the Pu^{238} half life. This fact casts suspicion on the validity of the calculated back-scattering correction, although the error in the Np^{238} disintegration rate could be due to other factors. Because of this uncertainty, the back-scattering correction is believed to be uncertain and probably lies between 1.13 and 1.28. In the absence of further information, the average value 1.20 was used.

Correcting for zero-absorber extrapolation, decay scheme, geometry, and back-scattering, the disintegration rate per sample was found to average 309,000 dis/min (301,000 on tube 1 and 316,000 on tube 2). Using a half-life value of 1.32 days, this corresponds to 8.5×10^8 atoms of Pa^{232} at the end of the bombardment.

2.4 Amount of Pa^{231} Bombarded. The alpha counts of an aliquot of the Pa^{231} solution were measured to determine the amount of Pa^{231} bombarded. Because there was later some suspicion that the resulting value might be incorrect, the samples that were used for counting the Pa^{232} were dissolved and analyzed for Pa^{231} , as described in Sec. 2.2. Although the results checked within 5 per cent of the original value, the results of the analysis were used to give the value of $N_B = 0.0369 \mu\text{g}$ of Pa^{231} (1920 c/min).

3. NEUTRON FLUX

3.1 Equations and Definitions. The development of the equations to be used here has been discussed elsewhere⁹ and will be summarized here.

$n(E)$ = neutron density as a function of the energy E of the neutrons

T = "temperature" of the neutrons

v = velocity of neutrons of energy E ($v = \sqrt{2E/m}$)

n = total neutron density

$n(E)v$ = neutron flux of "monochromatic" neutrons of energy E (4)

$\sigma(E)$ = cross section per atom as a function of E

$E_0 = 0.025 \text{ ev}$ (energy for which $v = v_0 = 2200 \text{ meters/sec}$)

$T_0 = 293^\circ\text{K}$ (temperature at which $kT = E_0$)

σ_0 = value of $\sigma(E)$ at energy E_0

The thermal part of the neutron distribution may be approximately expressed as a Maxwellian distribution:

$$n(E) dE = \frac{2n}{\sqrt{\pi}} (kT)^{3/2} \sqrt{E} e^{-E/kT} dE \quad (5)$$

The total neutron flux for any distribution is

$$(nv)_{\text{tot}} = \int_0^{\infty} n(E) v dE \quad (6)$$

If the flux is entirely thermal, the total flux can be calculated from Eqs. 5 and 6, in which there is very little contribution to the integral beyond the Cd cut off (approximately 0.25 ev). The total thermal flux then is

$$(nv)_{\text{th}} = \int_0^{\infty} n(E) v dE = \frac{2n}{\sqrt{\pi}} \sqrt{\frac{2kT}{m}} \quad (7)$$

Using the notation of Eq. 3 for bombarded and produced nuclides, when the bombardment is constant, (i.e., the neutron density n is constant),

$$N_A = N_B t \int_0^{\infty} \sigma(E) n(E) v dE \quad (8)$$

It is often useful to use this equation in a nonintegral form (e.g., Eq. 3), and this is done by defining an average cross section ($\bar{\sigma}$), such that

$$N_A = N_B t \bar{\sigma} \int_0^{\infty} n(E) v dE = N_B t \bar{\sigma} (nv)_{\text{tot}} \quad (9)$$

If the bombarded nucleus absorbs only thermal neutrons, then an average thermal-neutron capture cross section may be defined by a corresponding equation:

$$N_A = N_B t \bar{\sigma}_{\text{th}} (nv)_{\text{th}} \quad (10)$$

Equation 10 may also be used when the bombarded nucleus will also absorb neutrons which are above thermal energies, but the bombarding neutrons are restricted to thermal energies (as in thermal columns).

Another useful concept is that of the average effective thermal-neutron capture cross section. This concept is convenient to use when most of the neutron capture occurs in the thermal-neutron region, but part of it occurs above this region. In this case, the flux considered is not the total flux but only the thermal-neutron flux, and the average cross section ($\bar{\sigma}'_{\text{th}}$) is defined by

$$N_A = N_B t \bar{\sigma}'_{\text{th}} (nv)_{\text{th}} \quad (11)$$

It should be pointed out that the average cross sections defined in Eqs. 9, 10, and 11 are functions of the temperatures of the thermal-

neutron distributions since both the capturing power of the nuclei and the neutron flux will vary with the neutron-energy distribution. Since the temperatures of the thermal neutrons depend upon the pile used for measurement, the value of the average thermal-neutron capture cross section may vary from pile to pile. However, if only thermal-neutron capture is involved, if the temperature of the neutrons in the various piles is known, and if the substance involved is a "1/v absorber," i.e., $\sigma(E) \propto 1/v$, then it is possible to compare cross sections by the relations

$$\sigma(E) = \sigma_0 \frac{v_0}{v} \quad (12)$$

$$\sigma_0(nv_0) = \bar{\sigma}_{th}(nv)_{th} \quad (13)$$

$$(\bar{\sigma}_{th})_{T_1} = \sigma_0 \frac{\sqrt{\pi}}{2} \sqrt{\frac{T_0}{T_1}} \quad (14)$$

where T_1 = temperature of pile 1.

If the activation due to nonthermal neutrons is not involved (e.g., by taking Cd differences), these equations can usually be used for comparison since the assumption of 1/v absorption within the thermal region is generally at least approximately true.

3.2 Measurement of Neutron Flux. A complete description of the method has been given by Jaffey and Magnusson.⁹ The method involved the measurement of the activity of a gold-foil monitor irradiated with the sample. The gamma activity of this foil was measured with an ionization chamber which had been calibrated with a similar gold foil exposed to a known neutron flux. The source of the absolute neutron-flux calibration was the so-called "standard" (sigma) graphite pile, which contained a Ra-Be neutron source whose total neutron emission had been independently measured. The accuracy of the absolute neutron-flux calibration depended, among other factors, upon the accuracy of the total neutron emission rate of this Ra-Be source, which was considered to be within ± 10 per cent. The activities of the gold foils bombarded in the standard pile and in the heavy-water pile were compared after correction for differences in cadmium ratios (due to resonance activation differences) and for the change in the average thermal-neutron cross section resulting from differences in the neutron temperatures of the two piles.

By this method, the neutron flux for this bombardment was found to be 11.5×10^{11} neutrons/sec/cm². Since the total bombardment time was 824 min, the total time-integrated thermal-neutron flux (nvt) to which the sample was exposed was 5.69×10^{16} neutrons/cm².

The neutron flux measured in this experiment corresponds to the $(nv)_{th}$ of Eq. 7 and refers only to the thermal part of the flux. Since no cadmium ratios were taken on the Pa^{231} activation, the cross section calculable from the data represents an average effective thermal cross section as defined in Eq. 11.

4. CALCULATION OF CROSS SECTION OF Pa^{231}

Since the half life of Pa^{232} is fairly short, it was necessary to correct for decay during bombardment. It can be readily shown that, for constant bombardment,

$$N_A = N'_A \frac{\lambda t}{1 - e^{-\lambda t}} = N'_A (1.158) \quad (15)$$

where N_A = total number of Pa^{232} atoms formed during time t (824 min)

N'_A = number of Pa^{232} atoms present at zero time (bombardment end)

$$\lambda = 0.000365 \text{ min}^{-1}$$

From Secs. 2.3, 2.4, and 3.2 and Eq. 15,

$$\begin{aligned} N_A &= 8.5 \times 10^8 \\ N'_A &= 9.6 \times 10^{13} \\ (nv)_{th} t &= 5.7 \times 10^{16} \end{aligned}$$

and substituting these into Eq. 11, the resulting value for the average effective cross section of Pa^{231} is

$$(\bar{\sigma}'_{th})_{400^\circ\text{K}} = 180 \text{ barns}$$

5. COMPARISON WITH OTHER RESULTS

Four other measurements^{14,15,19} have been made of the Pa^{231} capture cross section with quite discordant results. All the measurements involved another method of evaluating N_A (the number of Pa^{232} atoms formed) through the isolation of the uranium fraction by ether extraction and the alpha assay of the U^{232} formed through the decay of Pa^{232} . Table 1 summarizes the pertinent aspects of these measurements.

It should be pointed out that the cross sections measured by Sellers et al.^{15,19} are for 400°K thermal neutrons, since the value used for the cross section of the monitor (Np^{237}) was 172 barns, the average effective thermal-neutron capture cross section in the heavy-water pile.⁹ Within the approximation that only thermal activation occurs

and that both the monitor and sample are $1/v$ absorbers, it can easily be shown from Eqs. 10 and 14 that no matter what the actual temperature of the pile thermal neutrons the cross section measured is for the temperature at which the monitor cross-section value was measured. However, since epithermal activation was not excluded either in the sample or in the monitor, the cross section calculated from Eq. 11 is not necessarily the effective thermal cross section that would have been measured in the heavy-water pile because of the difference in neutron-energy distributions and the resulting probable difference in epithermal neutron capture in the monitor and sample.

In view of the wide discrepancies found between these measurements, it might be worth while to evaluate possible sources of error in each experiment.

In the Van Winkle measurements,¹⁴ the efficiency of extraction of U^{232} from the Pa^{231} was not determined, except for that in the Clinton bombardment; the loss in the wash solutions was measured and found to be small. The presence of unsuspected uranium-complexing agents in the original solutions could have decreased the U^{232} yields, which could account for the low cross-section values.

The neutron-flux values were determined through previous calibrations of pile power versus flux and through the use of measured power dissipation during the bombardment time. The use of the calibration in the case of the heavy-water pile might have been somewhat in error owing to gradual changes in the power-flux conversion factor since the calibration time (about 2 yr previous) and owing to possible shadowing effects in the neighborhood of the thimble, resulting from neutron absorption by control rods and strongly absorbing samples in the thimble. Although these effects are in the correct directions to help explain the discrepancy in the cross-section values, no information is available as to the magnitude of these effects at the time of bombardment. In any case, it is probable that the decrease in flux possible would not explain the large discrepancy.

The flux in the Clinton bombardment was also determined from a previous power-flux calibration.^{12,13} The calibration was expected to have an error of 15 to 20 per cent because of uncertainties in the flux of the standard pile used, but it was probably also in error because of the neglect of resonance capture in the monitors used. Because of the difference in the resonance capture of the silver monitors in the standard pile and the reacting pile, the flux value resulting would be expected to be too high. This would be in the correct direction in explaining a low cross-section value. In addition, the pile loading was changed¹⁸ between the time of calibration and the time of measurement, which would change the flux distribution in the pile. It can only

be said that the Clinton flux had considerable uncertainty, with some possibility that it was too high.

The measurements of Sellers et al.^{15,19} may be considered somewhat more reliable than those of Van Winkle. Although the chemical yield of U^{232} was not determined in the Clinton bombardment, it was evaluated in the Hanford activation. The amount of U^{232} in the Pa^{231} was evaluated by alpha-particle-energy resolution in the multichannel pulse analyzer¹⁷ before extraction and compared with the yield of U^{232} from the separation process. Since the two values checked, there is assurance in this case as to the Pa^{232} yield. In both experiments, the errors in flux measurements would seem to depend primarily upon the accuracy of the accepted cross section⁹ of Np^{237} and upon the amount of error introduced by differences in resonance activation of Np^{237} in the two piles.

The Pa^{231} cross-section value reported here depends on a neutron-flux determination with a gold monitor. This procedure is identical with that used in determining the standard Np^{237} cross section⁹ used by Sellers et al., and the flux values derived are therefore at least as reliable as those deduced from use of the secondary Np^{237} standard. The error introduced through the uncertainty in the evaluation of the absolute Pa^{232} beta emission rate is unknown but is probably less than 20 per cent.

It may be that the resonance capture of Pa^{231} is large enough and sufficiently different in the various piles that comparison of the effective cross-section values between the heavy-water and graphite piles is not easily possible. However, assuming that such differences are smaller than the discrepancies found here, there is the problem of evaluating from these data an estimate as to the best value to use for the Pa^{231} cross section. Although Van Winkle's results are lower than the others and although it is possible to guess why low results could have been measured, the relative consistency of his two values makes it undesirable to discard them. In the absence of real criteria for evaluating the validity of the various determinations, a weighted average might be the most suitable value to use. Rather arbitrarily assigning the value 0.5 to each of Van Winkle's two values and the value 1 to the others, the averaged value for the average effective thermal-neutron capture cross section of Pa^{231} in the heavy-water pile was calculated to be about 200 barns.

6. DISCUSSION

It was not possible to calculate accurately the yield of U^{232} by the path in Eq. 2b, but, by using the known cross sections in Eqs. 1 and 2 and by assuming that (1) the cross sections for $U^{238}(n,2n)U^{237}$ and

$\text{Th}^{232}(n,2n)\text{Th}^{231}$ are about the same and that (2) the concentration of fast neutrons in the graphite capable of causing an $(n,2n)$ reaction is approximately 0.1 (the concentration in the uranium slugs), it is possible to calculate the $\text{U}^{232}/\text{U}^{233}$ activity ratio and to compare it with the ratio found for U^{233} produced in the thorium carbonate in the Clinton graphite pile²⁰ ($\text{U}^{233}/\text{Th}^{232}$ ratio = 30 ppm). The calculated $\text{U}^{232}/\text{U}^{233}$ activity ratio, 1.6×10^{-4} , checks very closely with the only experimental value.²¹ Within the limits of error of the experiments and calculations, it is probable that the path in Eq. 2b predominates just as it does in the Pu^{238} formation.

These results indicate that just as Pu^{238} will always be found in Pu^{239} made at high power levels, so will U^{232} be found in U^{233} made under these conditions. In the U^{233} case, it is possible to decrease the fast-neutron concentration by increasing the amount of moderator between the thorium blanket and the fissioning material, whereas this is not possible in the case of Pu^{239} formed in a natural uranium-graphite pile.

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Table 1—Pa²³¹ Capture Cross-section Measurements by Various Methods

Authors	Jaffey and Van Winkle	Van Winkle	Van Winkle	Sellers et al.	Sellers et al.
Report	This paper	ANL-4281	ANL-4281	ANL-4282	ANL-4282
Pile	Argonne heavy-water	Argonne heavy-water	Clinton graphite	Clinton graphite	Hanford graphite
Neutron-flux monitor	Gold-foil comparison to standard pile	Flux vs. power calibration	Flux vs. power calibration	Np ²³⁷	Np ²³⁷
Thermal-neutron temperature in pile*	400°K	400°K	550°K	550°K	550°K
Activity measured	Pa ²³² (betas)	U ²³² (alphas)	U ²³² (alphas)	U ²³² (alphas)	U ²³² (alphas)
Chemical yield determined	Not necessary	No	No	No	Yes
Average effective thermal-neutron capture cross section meas- ured,† barns	180	107	105	230	290
Neutron temperature for cross section given	400°K	400°K	550°K	400°K	400°K
Cross section corrected to 400°K, barns	180	107	123	230	290

*The temperature of the thermal neutrons in the Argonne heavy-water pile has been found to be 400°K,⁹ while that in the lattice of the Clinton graphite pile has been found to be 550°K.¹² The temperature of the neutrons in the Hanford graphite pile is probably not very different from that in the Clinton pile because of the similarity in construction.

†Resonance activation not measured for Pa²³¹.

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Paper 9.16a

SOME MEASUREMENTS OF THERMAL-NEUTRON CAPTURE
CROSS SECTION OF Pa^{231}

By Q. Van Winkle

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1. INTRODUCTION

After the discovery¹ that Pa^{231} had a fairly large thermal-neutron capture cross section, it was proposed that some U^{232} be made, for tracer purposes, by irradiating Pa^{231} in a pile and allowing the Pa^{232} formed to completely decay. Samples of Pa^{231} were irradiated in the Chicago heavy-water pile and in the Clinton pile for this purpose, and the U^{232} was extracted. Although the experiments were not designed for the purpose of measuring the Pa^{231} capture cross section, some values could be calculated from the U^{232} yield, provided the neutron flux was known. Values for the neutron flux were secured from the pile operators, and the cross section was evaluated as described below.

The capture cross section (σ) of a nucleus may be defined by the equation

$$N_1 = N_2 \sigma \quad nvt \quad (1)$$

where N_1 = number of nuclei changed by the bombardment

N_2 = number of target nuclei

nv = neutron flux during the bombardment time t

2. EXPERIMENTAL WORK

In the first bombardment, 0.23 mg of Pa^{231} in the form of the oxide was sealed in a quartz tube and bombarded for a little over 4 days

in the thimble of the Argonne heavy-water pile. After removal of the sample from the pile, the Pa^{232} was allowed to decay completely, the Pa^{231} was dissolved, and the U^{232} was extracted.

In order to convert the Pa^{231} to a soluble form, the sample was slurried out of the quartz tube with 8N nitric acid, evaporated to dryness, and then treated with concentrated HF. After drying, the U^{232} was extracted from the Pa^{231} by the following procedure:

The sample was taken up in nitric acid, and the solution was made 10N in ammonium nitrate. Twice the volume of ether was shaken with the solution, which should have extracted about 75 per cent of the U^{232} into the ether layer. After separation of the ether layer, three more such equilibrations of the original solution were made, each process presumably removing about three-fourths of the remaining U^{232} . Each ether sample was then treated twice with equal volumes of a wash solution containing 0.1N nitric acid and 10N ammonium nitrate in order to remove traces of Pa^{231} . The same wash solutions were used for all the ether samples in order to minimize loss of uranium into the washes, and for the same reason the ether layers were washed in the order of uranium concentration (i.e., first ether layer washed first, etc.). By this method, over 95 per cent of the U^{232} should have been extracted into the ether layers with none of the Pa^{231} , provided no disturbing factors were present such as uranium-complexing agents (e.g., sulfate). This matter was not tested, however, and the U^{232} was extracted from the ether by equilibrating the ether layers with equal volumes of plain water.

All the water layers from the ether extraction were combined and evaporated to a small volume, and the entire sample was mounted on a plate.

This sample was found to contain 60,700 c/min in an alpha counter. Correcting for possible 5 per cent loss of uranium in the wash solutions, the irradiation yield would be 63,900 c/min. The sample was analyzed with an alpha-energy pulse analyzer,² and it was found that only the U^{232} peak was evident, indicating reasonably good separation from Pa^{231} . The total number of atoms of U^{232} on the plate (assuming complete chemical extraction) is equal to the number of Pa^{232} atoms formed during the bombardment, decay of the U^{232} being negligible. To translate the counting rate of the U^{232} into the amount present, the U^{232} half-life value was taken as 70 ± 3.5 years.^{3,4} The total number of U^{232} (and hence Pa^{232}) atoms formed, using 52 per cent as the geometry of the alpha counter, was found to be 6.53×10^{12} .

The amount of Pa^{231} used was measured prior to the bombardment by counting the number of alpha particles emitted from a known fraction of the total sample. Using the value 5.17×10^4 c/min/ μg of Pa^{231}

determined⁵ for the 52 per cent geometry, the weight of Pa^{231} was found to be 0.231 mg or 6.02×10^{17} atoms.

In a second bombardment, 1.23 mg of Pa^{231} was precipitated as the hydroxide, dried to an oxide, and enclosed in a platinum thimble, which was then bombarded in the Clinton graphite pile for about a month. After decay of the Pa^{232} , the U^{232} was extracted as described above. Although no check was made on the amount of uranium left in the original Pa^{231} solution, the wash solutions were checked and found to contain 5 per cent of the total U^{232} extracted. Correcting for this loss, the total counting rate of the U^{232} was found to be 1.13×10^7 c/min, which corresponds to 11.54×10^{14} atoms of Pa^{232} formed.

The amount of Pa^{231} used was measured both before and after the bombardment, using alpha assay as the analytical method. Both measures gave the value 1.23 mg, which corresponds to 3.21×10^{18} atoms.

3. NEUTRON-FLUX DETERMINATION

The equations and definitions pertinent to the discussion have been developed elsewhere⁶ and have also been summarized by Jaffey and Van Winkle.¹

The neutron-flux determination at the Argonne heavy-water pile depended upon two factors: (1) the measured power dissipation of the pile during the time of bombardment and (2) the calibration of flux versus power carried out about 2 yr previous. The log of the pile operator showed that the sample received a bombardment corresponding to 7660 kw-hr. A calibration made by Wattenberg⁷ and corrected by Jaffey and Magnusson⁸ gave the calibration factor as 300 kw, equivalent to 11.0×10^{11} neutrons/sec/cm². Thus the total bombardment was equivalent to 10.1×10^{16} neutrons/cm².

As described by Jaffey and Van Winkle,¹ this was a thermal-neutron flux for a pile temperature of 400°K (the temperature of the heavy-water pile).

The neutron-flux determination for the Clinton pile depended upon the same two factors. The log kept by the pile operator⁸ showed that the sample was irradiated in a position at which the flux was 60 per cent that at the center of the pile during a time in which the integrated total pile power was 3,157,000 kw-hr. The pile calibration has been described by Jones et al.⁹ Using the neutron density reported there (1.47 neutrons/cm³/watt) and the appropriate "average" velocity (3.40×10^5 cm/sec), the thermal flux at the center of the pile was found to be 5.00×10^5 neutrons/sec/cm²/watt. The average velocity was calculated by the use of the equations described by Jaffey and Van Winkle¹ and a neutron "temperature" of 550°K.⁹ At the position of bombardment, the neutron flux was then 3.0×10^5 neutrons/sec/cm²/

watt. With this calibration value, the integrated thermal-neutron flux for the entire bombardment was found to be 3.41×10^{18} neutrons/cm². The calibration may have had three sources of error: (1) adequate corrections were not made for resonance capture in the monitors used, (2) the neutron emission of the Ra-Be source used in the calibration was uncertain between 10 and 15 per cent, and (3) the loading pattern of the pile was changed¹⁰ between the time of calibration and the time of bombardment, which may have introduced a change in the neutron-flux distribution.

4. CROSS-SECTION VALUES

Using the following values for the determinations (Secs. 2 and 3)—first bombardment: $N_1 = 6.5 \times 10^{12}$, $N_2 = 6.0 \times 10^{17}$, $nvt = 1.01 \times 10^{17}$; second bombardment: $N_1 = 1.15 \times 10^{15}$, $N_2 = 3.21 \times 10^{18}$, $nvt = 3.4 \times 10^{18}$ —and substituting these values into Eq. 1, the cross-section values are $\sigma = 107$ barns for the Argonne heavy-water pile, 400°K, and $\sigma = 105$ barns for the Clinton graphite pile, 550°K.

The two values are not directly comparable, but if it is assumed that the resonance capture of Pa^{231} in both piles is negligible the values may be corrected for the neutron temperature differences. Using the equations described by Jaffey and Van Winkle,¹ the second value may be corrected to 400°K and may be found to be 123 barns. For the same temperature (400°K) the two measurements lead to the cross-section values $\sigma = 107$ barns for the Argonne heavy-water pile and $\sigma = 123$ barns for the Clinton graphite pile.

A discussion of other measurements of this cross section may be found in Paper 9.16.

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Paper 9.17

A SIMPLE ELECTRONIC DEVICE FOR MEASUREMENT OF SHORT HALF LIVES: THE HALF LIFE OF Em^{218}

By Martin H. Studier

[Editor's Note: Contribution from the Argonne National Laboratory.
Based on Report CC-3790. Prepared for publication Mar. 12, 1947.]

ABSTRACT

A simple electronic device consisting of a series combination of a resistor and condenser, a standard alpha counter, and an oscilloscope has been devised to measure short half lives. The half life of Em^{218} has been determined as 0.019 sec.

1. INTRODUCTION

During the investigation of the protactinium radioactive decay series¹ and the $(4n+1)$ series,² alpha emitters with half lives of less than 1 sec were found. Since chemical isolation was not possible, indirect methods were necessary to determine the periods of the isotopes. A simple electronic circuit which can be used to measure the time intervals between the emissions of successive alpha particles was devised. In the decay chain $A \xrightarrow{\alpha} B \xrightarrow{\alpha} C$, let A be the (long-lived) parent of B, the half life of which is to be measured. The instant that the atom A emits an alpha particle the atom B is formed, and the time elapsing until B emits an alpha particle is the lifetime of B. An average of a number of measured time intervals between the successive disintegrations of A and B gives the mean life of B which is equal to $1/\lambda$ where λ is the decay constant of B. The half life is then given by $0.693/\lambda$.

2. EXPERIMENTAL WORK

A schematic diagram of the circuit which was used for the measurement of the short time intervals between pulses is shown in Fig. 1. A resistor R_1 in series with a condenser C_1 was connected between the plate and cathode of one of the tubes T_1 in the first trigger pair in the scaling circuit of a standard alpha counter. The horizontal deflecting plates of an oscilloscope were connected across the condenser C_1 and through a potentiometer P which was included in the circuit to control the horizontal position of the fluorescent spot on the oscilloscope screen. The scaling pair was of the Eccles-Jordan type³ with 6C5 triode tubes. Such a trigger pair exhibits two stable states in which one tube is conducting while the other is nonconducting. A pulse fed to the grids of the pair will cause the tubes to reverse from the one stable state to the other in a few microseconds. Because of the potential drop across the plate resistor, the plate voltage of a tube in the conducting state is much lower than that in the nonconducting state. When a pulse is fed to the grids of the scaling pair, there is a sudden change in the plate voltage of tube T_1 which is reflected in a change in voltage across condenser C_1 .

The circuit was operated as follows: The potentiometer P was adjusted until the fluorescent spot was at the extreme right of the oscilloscope screen when tube T_1 was in the conducting state. A pulse caused by alpha disintegration in the ionization chamber of the counter caused tube T_1 to change to the nonconducting state with a consequent sudden rise in plate voltage. Condenser C_1 charged through R_1 and R_2 at a rate dependent on the time constant $(R_1 + R_2)C_1$. As the voltage across the condenser increased, the spot moved across the screen. If another alpha disintegration occurred during the period of the sweep, the stable states of the trigger pair again reversed and the spot returned to its original position as the condenser discharged. The distance that the spot traveled across the screen was a measure of the time interval between the two successive alpha disintegrations. Such "coincidences" were observed visually with the aid of a calibrated screen. A sine wave from an oscillator was put in the vertical deflecting plates of the scope to give a moving band which was more easily observed than a moving spot. Resistor R_1 and condenser C_1 were so chosen that the period of the sweep was about 0.2 sec. If a single alpha disintegration occurred, the spot moved across the screen and off the other side. It could be brought back to its original position by shorting out condenser C_1 with the switch S .

A time calibration of the sweep is dependent on the time constant of the circuit, the voltage difference between the conducting and noncon-

ducting states of tube T_1 , and the sensitivity of the oscilloscope. The time constant $(R_1+R_2)C_1$ was 0.1658 sec, the voltage difference was 235 volts, and the sensitivity of the oscilloscope was 43 volts/in. The equation for the instantaneous potential difference between the horizontal deflection plates of the oscilloscope was

$$v = 235(1 - e^{-t/0.1658})$$

From the above equation and the sensitivity of the oscilloscope a calibration curve was constructed relating time with sweep distance.

It is necessary to consider the possibility of chance coincidences between alpha particles arising from the background of the sample and counter. The relative number of such random coincidences can be minimized by using low-counting-rate samples and low-background counters. Although it may not be feasible to completely eliminate the background effect, corrections can be made for random coincidences. Since the time distribution of particles emitted from a long-lived radioactive substance is purely random, the probability that n particles arrive in time t is given by the Poisson equation,

$$W_n = \frac{x^n e^{-x}}{n!}$$

where x is the average number of particles which arrive in time t . In the experimental apparatus the emission of an alpha particle starts the sweep on the oscilloscope. Since for a purely random distribution the probability of a future event is not affected by the previous occurrence of an event, the chance that another particle arrives during the period of the sweep is given by the Poisson equation. Thus it is only necessary to determine the number of random alpha disintegrations to correct for random coincidences.

In order to obtain a high ratio of true coincidences to random events a high geometry factor is essential. A geometry factor approaching 100 per cent was obtained by mounting the samples on a very thin film of Zapon supported on a 0.002-in. wire ring about 1 cm in diameter. The samples were supported in a vertical position between the parallel plate electrodes of the ionization chamber of the counter.

The half life of Em^{218} was obtained by measuring the time interval up to 0.2 sec between successive alpha particles from a sample of U^{230} in equilibrium with its daughters. The decay chain is as follows:¹

The half life of RaC' is so short that in most cases the arrivals of alpha particles from Em^{218} and RaC' were recorded as a single event. When the pulse due to the RaC' alpha particle was resolved it resulted in "triple" coincidences; thus if the Ra^{222} alpha particle starts the sweep, the Em^{218} alpha particle reverses it, and the RaC' alpha particle reverses it again. Only about 3 per cent of the total observed coincidences were such triple coincidences, and they were neglected. It can be seen from the above decay chain that half of the alpha particles will be observed as true $\text{Ra}^{222} - \text{Em}^{218}$ coincidences. The half life of Ra^{222} is so long by comparison with the sweep time that relatively few $\text{Th}^{226} - \text{Ra}^{222}$ coincidences occur. Those that do occur will result in triple coincidences. The total random counting rate is that due to U^{230} and Th^{226} , or half the total counting rate. (The background of the counter was negligible.) Since two alpha particles are involved in each coincidence, the total number of random events will be twice the number of coincidences. The average total disintegration rate of the sample was 12.3 per minute. The probable number of random coincidences was calculated for the observed time intervals and subtracted from the recorded number of coincidences. The correction varies almost linearly with time over the range represented by the period of the sweep. About 4 per cent of the total coincidences observed within 0.2 sec were estimated to be due to random events.

Figure 2 shows the frequency distribution of the observed time intervals after correction for random events. The total number of observed coincidence periods equal to or less than a given time interval is plotted against the time interval. The integral curve so obtained is exponential within the errors of the experiment and represents the decay of Em^{218} . The mean interval is 0.027 sec corresponding to a half life of 0.019 sec.

The same value was obtained by the following graphical analysis. Since the maximum interval observed is greater than 10 half lives of Em^{218} , essentially all the coincidences which occurred were observed. By subtracting N_t (the number of coincidences observed within a given time interval) from N_∞ (the total number of observed coincidences) and plotting this number $N_\infty - N_t$ against the time intervals on semilogarithmic paper, a straight line was obtained as shown in Fig. 3. The slope of the line is a measure of the half life of Em^{218} .

It is difficult to evaluate the reliability of the above data because of the uncertainty of the human error involved in the observations. However, it is believed that the half life is not in error by more than 0.002 sec.

The apparatus described above was also used to determine the half life of At^{217} (0.017 sec). The details of the experiment are described in another paper.²

Fig. 1 — Diagram of electronic circuit used to measure short time intervals between successive pulses.

Fig 2—Integrated frequency distribution of $\text{Ra}^{222}\text{-Em}^{218}$ coincidences representing the exponential decay of Em^{218} .

Fig. 3—Decay curve of Em^{218} .

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Paper 9.18

HALF LIFE OF Th^{227} (RADIOACTINIUM)

By S. Peterson and Albert Ghiorso

[Editor's Note: Contribution from the Argonne National Laboratory. Based on Report CB-3791. Prepared for publication Mar. 10, 1947.]

ABSTRACT

Direct decay of Th^{227} has been measured by periodical purification from daughters of portions of a solution containing Th^{230} and by measuring the ratio of the two activities with the pulse analyzer. The half life is 18.6 ± 0.1 days.

Because of the complicated growth and decay of activity in samples of Th^{227} (RdAc), previous measurement of the half life¹ has depended upon an involved mathematical analysis of carefully determined activity-time curves. Use of the multichannel differential pulse analyzer² which can measure individual alpha activities in a mixture affords a method with fewer inherent errors.

Since the alpha-particle energies of Th^{227} overlap those of its daughter Ra^{223} (AcX), simply following decay of Th^{227} using the pulse analyzer is unsatisfactory. However, samples of the activity mixed with isotopic standards can be purified from daughter activities with measurable yields and thus afford a good measure of the rate of decay.

Thorium iodate was precipitated from an approximately 3M nitric acid solution containing tracer activity of Th^{227} and long-lived Th^{230} (ionium). The precipitate was dissolved in nitric acid through the use of sulfur dioxide and reprecipitated with iodic acid to purify from isotopes of radium and actinium. The second precipitate was dissolved and diluted to a thorium concentration of 0.5 g per liter in 3M nitric acid. Eleven times over a period of 76 days, the tho-

rium was precipitated from a 50-microliter portion of the solution, and each sample was reprecipitated a sufficient number of times to ensure complete separation from isotopes of radium. Table 1 gives the results obtained in this series of experiments.

The final iodate precipitate was mounted on a platinum disk, and the alpha particles from Th^{227} and Th^{230} were counted simultaneously in the pulse analyzer. The ratio of the two activities was found both graphically and by least-squares analysis to decrease exponentially with a half life of 18.6 ± 0.1 days.

Table 1—Decay of Th^{227} Activity
in Sample Containing Th^{230}

Time, days	$\text{Th}^{227}/\text{Th}^{230}$ ratio
1.01	1.654
4.17	1.420
7.15	1.309
11.13	1.121
15.04	0.9835
19.10	0.8464
31.1	0.5327
40.0	0.3859
50.0	0.2663
62.2	0.1676
76.1	0.0979

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THERMAL-NEUTRON FISSION PROPERTIES OF Th^{227}

By S. Peterson and Albert Ghiorso

[Editor's Note: Contribution from the Argonne National Laboratory. Based on Report MB-IP-352. Prepared for publication Jan. 27, 1949.]

ABSTRACT

The thermal-neutron fission cross section has been determined for Th^{227} as $\left(1000 \begin{smallmatrix} +1500 \\ -500 \end{smallmatrix}\right) \times 10^{-24} \text{ cm}^2$.

A preliminary study has been made of the thermal-neutron fission properties of Th^{227} (radioactinium, 18.9-day alpha emitter). The Th^{227} was separated by coprecipitation with zirconium iodate, concentrated on cerous fluoride, and finally purified by extraction into a solution of thenoyl trifluoroacetone (TTA) in benzene. The sample was evaporated on a 2-mil platinum foil for fission measurements.

Fission measurements were made in the thermal column of the Argonne heavy-water pile using the high-sensitivity fission-counting apparatus described by Ghiorso and Bentley.¹ The fission rate of the sample was compared with that of a standard thin sample of Pu^{239} measured under identical neutron-flux conditions. The thermal nature of the neutrons was confirmed by repeating measurements with the fission chamber enclosed in a cadmium shell 0.027 in. thick. Under these conditions fission rates were reduced by a factor of 100 or more.

The results of a number of measurements of Th^{227} samples are given in Table 1. The weight of Th^{227} present in each sample was calculated from the disintegration rate and half life. Thermal-neutron fission cross sections were calculated using a value of $765 \times 10^{-24} \text{ cm}^2$ (reference 2) for the thermal-neutron fission cross section of Pu^{239} . The method of calculation is illustrated as follows for the first entry in Table 1.

$$\sigma(\text{fiss}) = \frac{235 \times 227}{0.880} \times \frac{1}{386 \times 239} \times 765 \times 10^{-24}$$

$$= 500 \times 10^{-24} \text{ cm}^2$$

The earlier measurements on samples 1 and 2 are obviously less reliable because of higher backgrounds and lower sensitivity of the fission-counting apparatus. There is an apparent increase in cross section with decay of the Th^{227} . This cannot be attributed to a high fission cross section of the daughter Ra^{223} , however, because measurements have set an upper limit of $100 \times 10^{-24} \text{ cm}^2$ for this cross section. Because of low counting rates and thick samples (high fission fragment self-absorption) the experimental error in these measurements was quite high, and limits on the thermal-neutron fission cross section have been set at $\left(1000 \begin{smallmatrix} +1500 \\ -500 \end{smallmatrix}\right) \times 10^{-24} \text{ cm}^2$.

ACKNOWLEDGMENTS

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Table 1—Fissionability of Th^{227} Samples

Sample No.	Time since purification, days	Weight of Th^{227} ($\times 10^{-12}$ g)	Fission, c/min			$\sigma(\text{fiss}) \text{ Th}^{227}$ ($\times 10^{-24} \text{ cm}^2$)
			Back-ground	Net total	Per 10^{-9} g of Pu^{239}	
1		880	510	235	386	500
2	1	97	338	200	1530	980
2	1	97	105	77	1090	530
2	1	96	130	93	1150	610
2	11	22	50	280	8900	1040
2	21	15	40	491	8450	2810
3	9	33	50	280	8900	690
3	19	23	40	484	8450	1810

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Paper 9.20

HALF LIFE OF Pa^{232}

By A. H. Jaffey and Earl K. Hyde

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INTRODUCTION

The half life of Pa^{232} has been measured⁶ on samples of Pa^{232} prepared by two different reactions: $\text{Th}^{232}(\text{d},2\text{n})\text{Pa}^{232}$ and $\text{Pa}^{231}(\text{n},\gamma)\text{Pa}^{232}$. The half life was determined only incidentally in the course of other experiments and is of but limited accuracy. However, it is being reported here because a value of greater accuracy has not as yet been published.

Both samples of Pa^{232} had long-lived contaminants which had to be subtracted in order to get the Pa^{232} half life. In the bombardment of Th^{232} , Pa^{233} was also formed by the reactions $\text{Th}^{232}(\text{d},\text{p})\text{Th}^{233} \xrightarrow{\beta} \text{Pa}^{233}$ and $\text{Th}^{232}(\text{d},\text{n})\text{Pa}^{233}$. The long-lived activity in the Pa^{232} formed by the $\text{Pa}^{231}(\text{n},\gamma)$ reaction was due to the Pa^{231} itself. Because Pa^{231} has two alpha particles with energies differing by about 300 Kev,¹ the difference in energy is released in the form of gamma rays, which are partially converted. Thus Pa^{231} gives a rather sizable amount of activity on the Geiger-Mueller counter.

1. EXPERIMENTAL WORK

The purpose of the first experiment was to examine the products of the deuteron bombardment of thorium. Some thorium metal was bombarded with about 20-Mev deuterons at the Berkeley cyclotron. The protactinium fraction was chemically isolated by several repetitions of a solvent-extraction separation using diisopropyl ketone to extract the protactinium. The chemical operations are discussed in greater detail elsewhere in this volume.² The decay of samples prepared at

each stage of the separation was followed on a mica-window Geiger-Mueller counter.³

The second experiment involved the bombardment of Pa^{231} with neutrons in the center of the Argonne heavy-water pile in order to determine the $\text{Pa}^{231}(n, \gamma)$ cross section.⁴ In this case, the cross section was so large that the amount of extraneous activity due to the slight fission of Pa^{231} was considered negligible, and no purification was carried out. Aliquots were counted, and the decay was followed with a mica-window Geiger-Mueller counter. Toward the end of the decay of the Pa^{232} , the Geiger-Mueller tube started to fail, and the decay curve was continued with a new mica-window Geiger-Mueller tube. It was possible to count the samples on both tubes several times before the first tube finally failed. The ratio of these counts was used to correct the data subsequently taken with the second tube. The tails of the decay curves consist of data taken with the second tube corrected to what they presumably would have been had the first tube been used. This procedure may have been slightly in error owing to the difference in window thicknesses (3.4 and 2.7 mg/cm², respectively) and other possible differences. However, since the Pa^{231} contributed only a small fraction of the initial count, a slight error in the measurement of its activity would hardly affect the half-life determination.

Because of their high initial disintegration rate, the samples were at first counted on the second shelf of the standard Geiger-Mueller tube support,³ and later, as they decayed further, they were counted on the first shelf. The second-shelf counts were normalized to the first shelf by taking several ratios between the counts at the first- and second-shelf positions at times when the counting rates were suitable.

In both experiments, the resolution losses were corrected for, and the split-pair technique described by Kohman⁵ was used to evaluate the properties of the Geiger-Mueller tubes. The Geiger-Mueller tubes used were the brass-walled mica-window type described elsewhere,³ which were quenched by Neher-Harper circuits. These were used with the Cyclotron Specialties Company scaler.

2. RESULTS

For the Pa^{232} samples coming from the thorium-plus-deuteron bombardment, the half-life values determined were somewhat less precise than those determined from the decay of pile-produced Pa^{232} , i.e., the deviation of the points from the straight line was greater. Table 1 shows the half-life values for various samples, while Fig. 1 shows the decay of a typical sample.

There is no evidence that more than one purification cycle was necessary for isolating the protactinium fraction. A decay curve obtained on an unpurified sample showed no clean decay: The apparent half life changed with time. This was probably due to deuteron-induced fission activities.

For the Pa^{232} formed by the $\text{Pa}^{232} (n, \gamma)$ reaction, Table 2 shows the half-life values for various samples, and Fig. 2 shows the decay of a typical sample.

The deviations shown in each table represent the mean deviation of the individual values from the average. The two values for the half life are 32.3 ± 0.4 hours (from $\text{Th}^{232} + d$) and 31.2 ± 0.2 hours (from $\text{Pa}^{231} + n$). Although the data in Table 2 are more precise, both half-life values are averaged since there is the possibility of consistent errors in either measurement.

The half life from these experiments may be taken to be 31.7 hr or 1.32 days.

3. RESULTS OF OTHER EXPERIMENTS

The half life of Pa^{232} was first reported by Gofman and Seaborg to be 1.6 days. Their Pa^{232} was formed⁶ by deuteron bombardment of Th^{232} in the Berkeley cyclotron and was purified by two complete cycles, each cycle involving precipitation with zirconium phosphate, solution in HF, and low-temperature precipitation with zirconium hydroxide. The protactinium was finally electrolyzed onto a copper cathode. The longer half life found in this experiment may have been due to incomplete separation from fission products or activities formed from impurities in the thorium. It has been found in this laboratory that purification with diisopropyl ketone is more effective in purifying protactinium from such radioactive impurities than precipitation with zirconium carriers.

Pa^{232} has also been made⁷ by the reaction $\text{Pa}^{231} (d, p) \text{Pa}^{232}$, and the half life was found to be 33 hr. In view of the fact that this determination of the half life was complicated by the presence of the two long-lived impurities Pa^{230} (17.7 days) and Pa^{231} , the agreement with the present experiment is quite satisfactory.

Table 1 — Half-life Values from Pa^{232} Formed by Th^{232} (d,2n)

Number of purification cycles involving di-isopropyl ketone extraction	Half-life values for various samples, hr	Relative precision* of decay curve	Average value for half life, hr
1	32.0	Good	32.3 ± 0.5
	31.5	Fair	
	33.3	Good	
2	32.3	Good	32.4 ± 0.3
	32.3	Good	
	33.4	Fair	
	32.3	Good	
	32.0	Fair	
3	31.8	Good	31.8
			$32.3 \pm 0.4^\dagger$

*Represents the degree of coincidence of the points with the decay curve. Curves labeled "Good" are arbitrarily given twice the weight of those labeled "Fair."

†Direct average taken for all the decay curves without regard to purification cycles.

Table 2 — Half-life Values from Pa^{232} Formed by Pa^{231} (n, γ)

Half-life values for various samples, hr	Average, hr
31.4	31.2 ± 0.2
31.3	
31.3	
30.8	
31.3

Fig. 1 — Decay of Pa from $\text{Th}^{232} + d$ ($\text{Pa}^{232} + \text{Pa}^{233}$).

Fig. 2 — Decay of activity from $\text{Pa}^{231}(n,\gamma)$ (Pa^{232}). (A) Total activity. (B) Pa^{232}

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Paper 9.22

IONIUM CONTENT OF A MIXED SAMPLE
OF IONIUM AND THORIUM.
PART OF A DETERMINATION OF THE HALF LIFE
OF IONIUM

By Winfred Rall and Arthur J. Dempster

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ABSTRACT

This paper describes the mass-spectrographic measurements of the ionium content in a mixed sample of ionium and thorium separated from uranium ores. One milligram of the oxide was used and two methods were employed—photometric measurement of the mass spectra and direct electrometer comparison of the ions collected.

Because ionium of mass 230 is an isotope of thorium of mass 232, preparations of ionium separated from uranium deposits are always mixed with unknown amounts of thorium. The half life has previously been deduced indirectly from the amount of radium formed in laboratory samples of purified uranium over a considerable period of time. Using four uranium samples that had stood for 15 to 20 years, Soddy deduced values of the half life of ionium varying from 72,000 to 78,000 years.

With the mass spectrograph, however, it is now possible to determine the percentage of ionium present in a mixed sample of ionium and thorium separated from uranium ores and thus to make possible the direct determination of the half life from the specific activity of the sample.

1. PHOTOGRAPHIC COMPARISON OF IONIUM AND THORIUM ISOTOPES

Doubly charged ions at masses 115 and 116 were photographed, and their intensities were compared by means of a Moll microphotometer with singly charged palladium ions at masses 104, 105, 106, 108, and 110 whose intensities are known from the accurate measurements of Sampson and Bleakney.

The accuracy of this procedure was checked by remeasuring the known intensities of the platinum isotopes in the same manner. The photographs were made in order to obtain a general idea of the relative intensities of the ionium and thorium isotopes and to see that no other ions were present that could complicate the electrometer comparison.

It turned out that the ratio was about 3 to 1, well-suited to photometric measurement, and, by good luck on the exposure time, a very good plate was obtained. The blackening curve for the plate drawn through the densities of the palladium ions is given in Fig. 1. The two densities for ionium and thorium are indicated and give a ratio of 2.75 to 1. This gives for the sample: ionium, 26.7 per cent; thorium, 74.3 per cent. The error is probably less than 3 per cent.

Test of the Photometric Procedure. The slope of the photographic blackening curve is known to depend on the mass of the ion and probably on the velocity. The curves drawn for the strontium and for the barium isotopes with lower velocity, taken from photographs on the same plate, show slightly different slopes.¹ Aston gives curves showing only a slight change for heavy ions from krypton to mercury. The velocity of the ions is given by $v = (e/m)r$, so that it is the same for the same radius of curvature r if the value of e/m is the same. Thus doubly charged thorium and platinum ions would be expected to have a blackening curve very close to that for singly charged palladium ions of half the mass. This was tested for platinum and found to be approximately true. The agreement of the slopes indicated that any error due to photometry is probably less than 4 per cent.

2. ELECTROMETER COMPARISON OF IONIUM AND THORIUM

After obtaining a good photograph for photometry, the rest of the 1-mg sample was used in making electrometer comparisons of the isotopes. Ions of the two masses were collected simultaneously in two Faraday chambers through a pair of slits 0.40 mm wide and spaced 0.88 mm apart (the separation of the two ion beams). The charges collected were observed by two new Lindemann electrometers and

exactly compensated by negative charges whose ratio was fixed by two four-dial resistance boxes. The ratio of the thorium to the ionium in nine readings and the percentages deduced are given in Table 1. The variations give an idea of the accuracy of the comparison.

No measurements were made of the scattered ions from one mass position to the other. If such scattering were present, the value for the percentage of ionium should be lowered perhaps to 26.0 per cent.

In general, the electrometer comparisons confirm the photometric measurements.

Table 1 — Results of Electrometer Comparison of Ionium and Thorium

	Th/Io ratio	Ionium, %	Thorium, %
	2.56	28.1	71.9
	2.78	26.5	73.5
	2.55	28.2	71.8
	2.90	25.6	74.4
	2.82	26.2	73.8
	2.80	26.3	73.7
	2.96	25.3	74.7
	2.82	26.2	73.8
	2.73	26.8	73.2
Av.	2.78	26.4	73.6

Fig. 1 — Thorium and ionium densities plotted on palladium blackening curve.

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ABSORPTION STUDY OF RADIATION CHARACTERISTICS
OF 6.8d U^{237}

By E. L. Brady and W. Robinson

An absorption curve of the radiations of U^{237} over the range 0.2 to 1,700 mg/cm² of aluminum has been resolved into four components: one γ (or x-ray) component and three β components with Feather ranges of 660, 60, and 22 mg/cm² of aluminum, corresponding to energies of 1.5, 0.25, and 0.12 Mev. A lead absorption curve has been resolved into three components with half-thicknesses of 4.8, 0.78, and 0.26 g/cm² of lead, corresponding to γ -ray energies of 0.53, 0.23, and 0.14 Mev.

The half-life of U^{237} has been found to be 6.8 ± 0.1 days.

1. INTRODUCTION

The product of the (n,2n) reaction on U^{238} , U^{237} was discovered in 1940 by Nishina, Yasaki, Ezoe, Kimura, and Ikawa,¹ who also established the mass assignment of 237. The maximum energy of the β radiations was reported to be 0.26 Mev by McMillan² from absorption data. As a first step in the study of the yield of U^{237} in fission material,^{3,4} a study of the radiation characteristics of this species was undertaken.

2. ISOLATION OF ACTIVITY

A disk of uranium metal about 2 in. in diameter and $\frac{1}{8}$ in. thick was bombarded with 16 Mev deuterons at the Berkeley cyclotron for 5,000 μ a-hr. The metal was then dissolved in HNO_3 , and portions were taken for analysis. It was found that after three precipitations as sodium uranyl acetate further reprecipitations caused no change in the absorption characteristics of the radiations in aluminum or lead. The conditions of precipitation were as specified by Connick et al.⁵

*This paper is reproduced direct from "Radiochemical Studies: The Fission Products," edited by Charles D. Coryell and Nathan Sugarman, National Nuclear Energy Series, Division IV, Volume 9, McGraw-Hill Book Company, Inc., New York, 1951. In that volume it appears as Paper 321. It is based on Report CC-724, June 21, 1943.

3. RESULTS

The activity observed with 13, 44.6, and 110.5 mg/cm² of total absorber (self-absorption, cellophane, air gap, and mica window amounting to 13 mg/cm², and aluminum absorbers of 31.6 and 97.5 mg/cm²) decayed with a 6.8d half-life* over a period of five half-lives. The UX₁ (Th²³⁴) activity was small compared to the activity available at the start of the measured decay period and was subtracted when it became appreciable compared to the 6.8d U²³⁷ activity. The decay curves are shown in Fig. 321.1.

A lead absorption curve of U²³⁷ was taken with 1,100 mg/cm² of aluminum above the sample at all times to reduce Bremsstrahlung; the lead absorbers were placed directly on top of the aluminum absorber. It was found that the observed intensity was not lowered when an aluminum absorber was also placed below the sample, and therefore the bottom part of the usual aluminum sandwich used in determining lead absorption curves was omitted. The curve obtained is indicated by A in Fig. 321.2. The hard component of this curve was assumed to be given by curve B, representing a half-thickness of 4.8 g/cm² of lead, which corresponds to a γ -ray energy of 0.53 Mev. On subtraction of curve B from the experimental points, there is obtained the set of points (triangles) through which curve C was drawn. This curve represents a half-thickness of 0.78 g/cm² of lead, corresponding to a γ -ray energy of 0.23 Mev. The residual activity (squares) is fairly well represented by curve D, which has a half-thickness of 0.26 g/cm² of lead, corresponding to an energy of 0.14 Mev. The counting ratio of these γ rays after correcting for absorption in the aluminum is 1:6:15.

An aluminum absorption curve taken over the range 13 to 1,700 mg/cm² of aluminum (Figs. 321.3 and 321.4) shows the presence of a γ (or x-ray component and two β components with Feather ranges of about 660 and 60 mg/cm² of aluminum, corresponding to energies⁸ of 1.5 and 0.25 Mev.† An aluminum absorption curve determined in the low-absorber counter⁷ over the range 0.2 to 22 mg/cm² of aluminum (Fig. 321.5) shows the presence of a still weaker component with a Feather range of 22 mg/cm², corresponding to an energy of 0.12 Mev. The counting ratio of these three components (in the order 1.5, 0.25, and 0.12 Mev) is 1:67:126.

*Editors' Note: The half-life of 6.8 days has been confirmed by A. Turkevich (Report CC-1331, Feb. 7, 1944) and C. W. Stanley, A. W. Adamson, and W. B. Leslie (Report CN-2833, June 16, 1945).

†Editors' Note: Later work on the radiations of 6.8d U²³⁷ is reported by D. W. Engelkemeir and A. Turkevich, Paper 322, this volume.

Fig. 321.1—Decay curves of U^{237} corrected for UX_1 activity. $\circ$, total absorber, 13 mg/cm². Δ , total absorber, 44.6 mg/cm². $\square$, total absorber, 110.5 mg/cm².

Fig. 321.2—Lead absorption curve of 6.8d U^{237} . $\circ$, original points, curve A. $\triangle$, curve B subtracted from curve A. $\square$, curve C subtracted from $\triangle$ points, curve D.

Fig. 321.3—Aluminum absorption curve of 6.8d U²³⁷; drawn on scale that shows the 1.5 Mev component. ○, original points. △, γ (or x-ray) background subtracted.

Fig. 321.4—Aluminum absorption curve of 6.8d U^{237} ; drawn on scale that shows the 0.25 Mev component. ○, original points. △, γ background subtracted. □, 1.5 Mev β component subtracted.

Fig. 321.5—Aluminum absorption curve of 6.8d U²³⁷; data taken in a low-absorber counter. O, original points. Δ, harder components subtracted.

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Editor's Note

In the references cited above, "this volume" refers to the volume of the National Nuclear Energy Series mentioned in the footnote at the beginning of this paper.

FURTHER STUDIES OF THE RADIATION
CHARACTERISTICS OF 6.8d U^{237}

By D. W. Engelkemeir and A. Turkevich

Studies of the nuclear radiations of 6.8d U^{237} by absorption in aluminum, copper, and lead, together with coincidence measurements, give proof of the presence of many conversion electrons accompanying the decay of this nuclear species. There appear to be 50, 220, and about 450 Kev γ rays, besides the x-rays of Np^{237} (about 14 and 95 Kev), and at least three nuclear particles are emitted, e^- of 0.1 and about 0.3 Mev and β^- of about 0.3 Mev. No simple decay scheme seems consistent with the admittedly crude data on the relative intensities.

1. INTRODUCTION

The use of the β -emitting 6.8d U^{237} to monitor nuclear reactions¹ as well as its frequent use as a uranium tracer has been continually handicapped by the presence of low-energy particles given off in the decay of this species. During the course of the applications of this activity for Project problems, some data were accumulated on the absorption characteristics of the radiations in various substances as well as a few measurements made with two Geiger-Mueller counters in coincidence. These data are presented here, although no decay scheme seems deducible.

The samples of U^{237} were prepared from pile-irradiated uranium and were purified from fission-product and Np^{239} activity by conventional chemical methods.¹ This procedure also purified the uranium of UX_1 (Th^{234}) and UX_2 (Pa^{234}); the specific activity, about 10^5 disintegrations per minute (dis/m) per milligram of uranium at the start, decayed with a 6.9d half-life over a 1-month period (Fig. 322.1).†

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†More extensive work² indicates that the half-life is 6.8 days.

The samples used for β -ray measurements were usually weightless or nearly so. However, for some of the γ -ray measurements, samples weighing as much as 0.8 g of uranium were used. In these samples, and toward the later stages of decay of the U^{237} , the observed activities were compared with samples of unirradiated uranium of

Fig. 322.1—Decay curve of U^{237} .

comparable weight and chemical treatment in order to correct for the contribution from UX_1 and UX_2 . For the coincidence work, the samples were frequently repurified by sodium uranyl acetate precipitation to free them from the UX_1 and UX_2 that had grown in.

2. PARTICLE-ABSORPTION CURVES

The absorption characteristics of the electrons were studied with two types of counting equipment. In the first case a conventional thin (2.7 mg/cm^2) end-window Geiger-Mueller counter was used with the sample on the top shelf and aluminum absorbers in the small space between the sample and counter. The sample was mounted on thin mica placed on cardboard. The aluminum absorption curves obtained on a sample containing about 1 mg of uranium separated from two irradiations performed 5 months apart were the same,

and both were in satisfactory agreement with the published curve of Brady and Robinson.² The absorption curves and their analysis ac-

Fig. 322.2—Aluminum absorption curve of U^{237} indicating γ background.

cording to usual methods of repetitive subtraction are given in Figs. 322.2 to 322.4.

Subtraction of the γ -ray background accentuates what may be interpreted as an x-ray (Fig. 322.3). This component was called a

“hard β ray” by Brady and Rubinson.² The interpretation as an x-ray is based on its low apparent intensity and on the fact that its absorp-

Fig. 322.3—Aluminum absorption curve of U^{237} after γ subtraction.

tion characteristics in aluminum (see below) agree quite well with those expected for the L x-rays of neptunium (about 14 Kev).

Subtraction of this component leaves what may be considered as the particle-absorption curve (Fig. 322.4). It appears to be complex. The main portion seems to have a Feather range of about 60 mg/cm² of aluminum and a corresponding energy of 0.25 Mev.

The particle-absorption curve has at least one softer component, which, on these curves, seems to blend into the main curve above

10 mg/cm² of added absorber. This soft component was investigated more thoroughly by use of the low-absorber counter³ constructed by

Fig. 322.4—Aluminum absorption curve of U^{237} after subtraction of the γ and x-ray components.

Raynor and Freedman. The combined results of two determinations, together with the result of a subtraction of the contribution of the 0.25 Mev β ray, are given in Figs. 322.5 and 322.6. This subtraction was made using a half-thickness of about 7 mg/cm² for the 0.25 Mev

Fig. 322.5—Aluminum absorption curve of U^{237} taken in low-absorber counter. $\circ$ and $\times$, original points from two experiments, curve A. $\bullet$, soft component, curve C (after subtraction of β component, curve B, from curve A), treated as a β component.

β ray, deduced from the more conventional type of absorption curve (Fig. 322.4).

It is noteworthy that there appear to be no particles cut out by the first 0.5 mg/cm^2 of absorber. This would indicate no very soft con-

Fig. 322.6—Aluminum absorption curve of soft component of U^{237} (curve C of Fig. 322.5) treated as an absorption curve of conversion electrons. Note that in this figure a linear scale is used for the ordinates.

Table 322.1—Summary of Absorption Measurements in Aluminum

Radiation	Energy, Kev	Counting ratio relative to β particles
Soft electrons, e^- , or soft β particles	80	1.8
	120	1.8
Main β particles, β^-	250	1.000
X-rays	13.4	0.019
γ component		0.004

version electrons. The range of the soft component would appear to be 20 mg/cm² if a Feather analysis is applied, corresponding to an energy of about 120 Kev (Fig. 322.5), or about 9 mg/cm² if it is interpreted as being due to conversion electrons (Fig. 322.6). The conversion-electron range corresponds to an energy of about 80 Kev, but this value must be considered as very uncertain.

The results of the absorption measurements of U²³⁷ in aluminum are summarized in Table 322.1.

Fig. 322.7—Aluminum absorption curve of U²³⁷. Carbon absorber against windows of counter.

3. PHOTON-ABSORPTION CURVES

Absorption curves were determined under special conditions in order to learn more about the electromagnetic radiation associated with the decay of U²³⁷. The experimental results follow.

3.1 Aluminum Absorption Curve. An aluminum absorption curve was taken with the counter window facing upward with enough carbon absorber against the window to cut out the main (0.25 Mev) β ray.

Fig. 322.8—Aluminum absorption curve of U^{237} after subtraction of γ component (Fig. 322.7).

After subtracting the γ component (Fig. 322.7), a photon component (Fig. 322.8) of about 90 mg/cm² half-thickness (about 15 Kev energy) remains. This is taken to be an x-ray of neptunium. Its counting ratio relative to the γ ray under these conditions is taken to be 1.48/2.55 or 0.58. Since, however, this curve was determined on a very heavy sample of U_3O_8 , the self-absorption of the x-rays must be considerable.

3.2 Lead Absorption Curve. A lead absorption curve was determined on the usual counting apparatus with the sample on the second shelf and absorbers on the first shelf until it could hold no more, and

Fig. 322.9—Lead absorption curve of electromagnetic radiation of U^{237} .

then the absorbers were put on the second shelf. Figure 322.9 indicates the resulting absorption curve and its analysis into a component of about 0.45 Mev as well as a very well established 0.22 Mev γ ray (Fig. 322.10). The slight upswing at the start of the latter curve is consistent with photons in the neighborhood of either 55 or 95 Kev.

The counting rates of the γ components, when corrected for absorption in the sample, are 2,000 (for the 0.22 Mev γ ray) to 60 (for the 0.45 Mev γ ray).

Fig. 322.10—Lead absorption curve of electromagnetic radiation of U^{237} after subtraction of hard γ ray (Fig. 322.9).

3.3 Copper Absorption Curves. Copper absorption curves were determined on the counter with the window facing upward with either an aluminum absorber (395 mg/cm^2) or a carbon absorber against the window to cut out the β rays. The sample used (as in the lead absorption curve) was very heavy, containing about 0.4 g/cm^2 of ura-

nium. The curve established with carbon against the window is indicated in Fig. 322.11, which shows its analysis into three components. The weakest of these was established more reliably from another curve with the aluminum absorber against the window. This, how-

Fig. 322.11—Copper absorption curve of electromagnetic radiation of U^{237} (carbon absorber used to absorb the β rays).

Table 322.2—Results of Absorption Measurements in Copper

Half-thickness, g/cm ²	Energy, Kev	Relative counting rate	Relative counting rate, corrected*
0.33	55	60	425
1.13	90	120	204
5.1	240	73	90

*Corrected for self-absorption in the sample and in the aluminum absorber.

ever, gave a poorer determination of the hardest component. The results of this analysis are summarized in Table 322.2, which also corrects the relative intensities for self-absorption in the sample. These data show that photons of both 55 and 90 Kev are present.

4. SUMMARY OF RESULTS AND DISCUSSION OF ORDINARY ABSORPTION CURVES

The relative intensities of four types of radiations, electrons, β rays, x-rays, and γ rays, corrected for sample absorption as well as for estimated counter efficiency (relative to β rays), are presented in Table 322.3. Because of the well-known difficulties of estimating efficiencies, it is possible that some of these results are in error by factors of 2 or 4.

Table 322.3—Relative Intensities of Various Components of 6.8d U^{237}

Component	Energy, Kev	Relative counting rates from absorption curves*			Relative counting rate from combined data	Relative counter efficiency	Relative intensities
		Al	Pb	Cu			
Soft electrons	80–120	1.8			1.8	1.0	1.8
β ray	250	1.0			1.0	1.0	1.0
X-ray	~14	0.019			0.019	0.006	3.1
γ ray	50			425	0.023	0.0015	1.5
X-ray	~95			204	0.011	0.0014	0.8
γ ray	~220	0.004	2000	90	0.005	0.003	0.17
γ ray	~450		60		1.5×10^{-5}	0.006	0.0025

*Corrected for absorption in the sample and in absorbers used to stop the β rays.

The long-held suspicion that the decay of U^{237} is accompanied by conversion electrons seems well established by these results. Not only is there definitely a soft component to the particle-absorption curve, but the photon-absorption curves have two components that can be identified with the K and L x-rays (14 and 95 Kev) of neptunium. The high intensity of the soft-particle component, as well as the great (quantitatively uncertain) yield of both K and L x-rays, means that the number of conversion electrons must be of the same order as the number of disintegrations.

Besides these x-rays, there appear to be photons of 50, 220, and 440 Kev that must be ascribed to nuclear processes. The high intensity of the 50 Kev radiation, as well as the apparent absence of electrons of energy less than 50 Kev, indicates that this radiation is unconverted and may be in series with all the disintegrations. This leaves the 220 and the 440 Kev γ rays to account for the conversion electrons. Their low intensity is compatible with having appreciable amounts of both converted. It is to be noted, however, that conversion of the 220 Kev γ ray in the K shell would give rise to electrons of

about 110 Kev (of about the same energy as the so-called "soft component" of the particle-absorption curves), whereas the 440 Kev γ rays would give rise to electrons of at least 330 Kev, about as hard as the "main-particle" component.

5. COINCIDENCE MEASUREMENTS

In view of the complexity of the radiation indicated by ordinary absorption measurements, it seemed desirable to check the results by means of coincidence-counting techniques. In particular, it was thought that the internal conversion of some of the nuclear γ rays evidenced by the presence of x-rays of neptunium might be confirmed if coincidences between the primary β ray and the conversion electrons were observed.

5.1 Particle-Particle Coincidences. (a) Experimental Arrangement of the Apparatus. The counters (Fig. 322.12a) were placed in such a way that the sample could "see" each counter, but the counters could not "see" each other. A lead sheet with a rectangular hole cut in one edge was placed between the two counters to reduce the scattering of particles from one counter into the other, which would give rise to spurious coincidences. The entire assembly was mounted inside a large shielded box from which the air could be displaced with helium in order to reduce the amount of absorbing material between the sample and the counters.

The counters were of the thin-mica-end-window type with brass shells $\frac{1}{16}$ in. thick; they were filled with 9.0 cm of argon and 1.0 cm of alcohol. The resolving time, t , of the counters and their associated circuits was 1.65×10^{-8} min. The efficiency of each counter was measured by counting a thin calibrated UX_1 - UX_2 sample in the standard position. The efficiencies of the two counters were the same and equal to 0.0172 after correcting for absorption of the UX_2 β particles.

The number of spurious coincidences due to scattering was estimated by placing samples of pure β emitters in the standard position and measuring the ratio of the coincidence rate to the sum of the single counting rates for β particles of different energies. This ratio was so small for a 0.25 Mev β particle (about 2×10^{-5}) that no correction was made for coincidences from this cause. Corrections were made for the cosmic-ray background and for the accidental coincidence rate which arises from the finite resolving time of the circuit.

(b) Results. When a thin sample (about 1 mg/cm²) of U^{237} is placed in the particle-particle coincidence arrangement, a large coincidence rate is observed which may be attributed to the simultaneous emis-

sion of two or more particles. The possibility that some of the observed coincidences are β - γ coincidences was considered. The counting efficiencies of the nuclear γ rays or the K or L x-rays observed in ordinary absorption measurements are much too low to account

Fig. 322.12a—Particle-particle coincidence arrangement. Distance from sample to counter, 4.0 cm; window 1, 4.0 mg/cm² of mica; window 2, 3.7 mg/cm² of mica.

Fig. 322.12b—Particle-photon coincidence arrangement. Distance from sample to counter 1, 0.8 cm; distance from sample to counter 2, 1.0 cm.

for the observed coincidences. The M x-rays of neptunium, because of their high absorption coefficients in argon, might be expected to have high counting efficiencies. Calculation of the efficiency of counter 1 on the basis of one M x-ray per disintegration leads to a

value which is too low by a factor of 4 to account for the high coincidence rate.

Experimentally, the possibility that a large fraction of the observed coincidences are between β rays and M x-rays is ruled out since no evidence is found for components in the particle-particle coincidence absorption curve which have half-thickness values approaching those expected for the more prominent M x-ray lines. The half-thickness values in aluminum for the most intense M x-ray lines are given in Table 322.4. The energies were obtained by extrapolation from the values for uranium.

Table 322.4—Estimated Absorption Characteristics of M X-rays of Neptunium

Line	Energy, Kev	Half-thickness in Al, mg/cm ²
M _{α_1}	3.26	1.17
M _{β_1}	3.43	1.36
M _{γ_1}	3.68	1.65

An aluminum absorption curve of the radiations entering one of the counters when the total absorber in the path of the other counter is kept fixed at 21.5 mg/cm² is given in Fig. 322.13. It represents the absorption curve of all radiations which are coincident with particles of range greater than 21.5 mg/cm² of aluminum. The complex absorption curve may be analyzed into two hard components of low intensity and two soft components of high intensity. The two hard components, D and E, can probably be attributed to photon-particle coincidences. Component D has a half-thickness of 67 mg/cm², corresponding to an energy of 13.8 Kev. This is probably the L x-ray of neptunium (13.9 Kev). Component E was drawn in quite arbitrarily. The slope that appears to fit the data best does not correspond to that found in any of the other absorption curves. Because of the uncertainty in the points obtained with thick absorbers, no significance is attached to the discrepancy. The two soft components are attributed to particle-particle coincidences because of their high intensities. Feather analyses give values of about 10 and about 80 mg/cm² for the ranges of components A and B.

Component A gives a very unsatisfactory Feather graph for range estimation, but it has the shape that would be expected for conversion electrons, which give a linear fall with amount of absorber. Accordingly, component A was replotted on a linear scale (Fig. 322.14). A straight line was obtained which extrapolates to give a range of 12 mg/cm². If only particle-particle coincidences are being ob-

served, components A and B are coincident with a third particle, C, with a range greater than 21.5 mg/cm^2 . Not much can be said about

Fig. 322.13—Particle-particle coincidence absorption curve of U^{237} . Constant total absorber of 21.5 mg/cm^2 of aluminum on counter 2. Thickness of absorber varied on counter 1. $\circ$, original points. $\square$, first subtraction. $\triangle$, second subtraction. ∇ , third subtraction. Vertical bars indicate standard deviation. Components A and B treated as β particles for Feather analysis.

the range of particle C except that it is probably so near that of particle B that it is not resolvable from the absorption curve. It should be noted that particles A and B may or may not be coincident.

5.2 Particle-Photon Coincidences. (a) Experimental Arrangement of the Apparatus. The two end-window counters used in the particle-particle coincidence experiments were placed face to face, with the

Fig. 322.14—Linear graph of the soft-particle component of coincidence absorption curves for range estimation. $\circ$, component A of Fig. 322.13. $\square$, component A of Fig. 322.15.

sample between them (Fig. 322.12b). The sample was evaporated on a thin-mica sheet which was mounted on a card with a circular hole larger than the sample cut in it. An absorber of sufficient thickness to stop the particles was placed between the sample and counter 2. The absorber was graphite if only particles were to be absorbed or aluminum if absorption of the L x-rays was also desired. Additional absorbers could be placed between the sample and either counter.

Fig. 322.15—Aluminum absorption curve of particle component of particle-photon coincidences in U^{237} . Constant absorber of $104 mg/cm^2$ of graphite on counter 2. Aluminum absorber added to counter 1. $\circ$, curve C, original points. $\bullet$, curve B, hard component subtracted. $\square$, curve A, component B (main β) subtracted. Components A and B treated as β particles for Feather analysis.

(b) **Results.** An aluminum absorption curve of the particles of the particle-photon coincidences is given in Fig. 322.15. A fixed absorber of 104 mg/cm² of graphite was kept against the window of counter 2, and aluminum absorbers were placed between sample and counter 1. The absorption curve was analyzed into two components having Feather ranges of about 13 and 74 mg/cm² which correspond to the

Fig. 322.16—Ratio of particle-photon coincidences to particle-counting rate in U^{237} for varying amounts of aluminum absorber added to particle counter.

two components observed in ordinary absorption curves and particle-particle coincidence absorption curves. As an alternative treatment, the softer component, A, is also plotted on linear scale in Fig. 322.14 (together with the A component of Fig. 322.13). A line with a definite curvature is obtained which seems to extrapolate to give a range of about 11 mg/cm².

A graph of the β - γ coincidences per β ray (Fig. 322.16) gives a straight line with a slight upward trend at low values of added absorber. If this trend is real it indicates that the low-energy particles are coincident with photons of higher counting efficiency than the high-energy particles.

An aluminum absorption curve of the γ radiation of the β - γ coincidences is given in Fig. 322.17. The total absorber between sample

Fig. 322.17—Aluminum absorption curve of photon components of particle-photon coincidences in U^{237} . Total absorber on counter 1, 5.0 mg/cm^2 (kept constant). Absorber on counter 2, 175 mg/cm^2 of graphite placed against the window. Aluminum absorbers placed between sample and graphite absorber. $\circ$, original points. $\square$, hard component subtracted.

and counter 1 was kept constant at 5.0 mg/cm^2 . The initial absorber against the window of counter 2 was 175 mg/cm^2 of graphite. Additional aluminum absorbers were placed between the sample and the

graphite. Subtraction of a hard component from the absorption curve gives a straight line showing a half-thickness of 90 mg/cm^2 , corresponding to an energy of 15.3 Kev. This component is probably the L x-ray of neptunium (about 13.9 Kev) arising from internal conversion of a γ ray in the K or L shell.

A copper absorption curve of the γ radiation of β - γ coincidences is given in Fig. 322.18. The total absorber between the sample and counter 1 was kept constant at 5.0 mg/cm^2 of copper. An initial absorber of 556 mg/cm^2 of aluminum was placed against the window of counter 2 in order to preferentially filter out the L x-rays. Additional copper absorbers were placed between the sample and the aluminum absorber. The absorption curve may be analyzed into two components with half-thicknesses of 200 and $1,620 \text{ mg/cm}^2$ of copper, corresponding to photon energies of 47 and 102 Kev. The 102 Kev component is probably the K x-ray of neptunium (about 100.2 Kev) arising from the K conversion of a γ ray.

A lead absorption curve of the γ radiation of the β - γ coincidences taken under the same conditions as the copper absorption curve is given in Fig. 322.19. The absorption curve may be analyzed into a component with a half-thickness of 73 mg/cm^2 (48 Kev) and another component with a half-thickness of 265 mg/cm^2 (80 or 140 Kev). The ambiguity as to the energy corresponding to a half-thickness of 265 mg/cm^2 arises since the region of the K-absorption edge of lead is involved. The number of points determined on this curve is too small to attach any great significance to the energy of the harder component. It is to be noted, however, that the same energy is obtained for the soft component as for the soft component in the copper absorption curve.

5.3 Discussion of Results of Coincidence Measurements. The presence of conversion electrons seems to be demonstrated quite conclusively by the results of the particle-particle coincidence measurements as well as by the presence of K and L x-rays of neptunium which are observed in both the ordinary and the β - γ coincidence absorption curves.

The particle-particle coincidence measurements can be interpreted on the basis of two particles, with energies of 0.09 Mev, A, and 0.30 Mev, B, and a third particle, C, with an energy between 0.12 and 0.30 Mev. The lower energy limit is set by the energy of a particle with a range greater than 21.5 mg/cm^2 , and the upper limit is set by the fact that no particles of energy greater than 0.30 Mev in appreciable intensity were detected. Since particle C had a transmission through 21.5 mg/cm^2 of absorber high enough to give a high coincidence rate

Fig. 322.18—Copper absorption curve of photon component's of particle-photon coincidences in U^{237} . Total absorber on the β counter, 5.0 mg/cm^2 (kept constant). Absorber on the γ counter, 556 mg/cm^2 of aluminum placed against window. Copper absorbers placed between sample and aluminum absorber. $\circ$, original points. $\square$, 102 Kev component subtracted.

with the particle of 0.3 Mev energy, its energy probably lies between 0.2 and 0.3 Mev. We must therefore consider the hard- β component of the ordinary β -absorption curve to be actually a mixture of two

components of nearly equal energy. Since particles B and C are coincident, at least one of them must be a conversion electron and must arise from K or L conversion of the 440 Kev γ ray or from L con-

Fig. 322.19—Lead absorption curve of photon components of particle-photon coincidences in U^{237} . Total absorber on the β counter, 5.0 mg/cm^2 (kept constant). Absorber on the γ counter, 556 mg/cm^2 of aluminum placed against window of γ counter. Lead absorbers placed between sample and aluminum absorber. $\circ$, original points. $\square$, 80 Kev component subtracted.

version of the 220 Kev γ ray. A high conversion coefficient for the 440 Kev γ ray would explain the low intensity of the 440 Kev γ ray and the high intensity of high-energy conversion electrons. Com-

ponent A could be the primary β ray, but it seems more likely that it is the K conversion electron of the 220 Kev γ ray and that either component B or C is the primary β ray.*

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*Editors' Note: Spectrometric measurements by L. Melander and H. Slätis [Phys. Rev., 74: 709 (1948); Arkiv Mat. Astron. Fysik, A36: No. 15 (1948)] give the energy of the β ray as ~ 0.23 Mev and the energies of the γ rays as 0.032, 0.057, 0.204, and 0.260 Mev.

Editor's Note

In the references cited above, "this volume" refers to the volume of the National Nuclear Energy Series mentioned in the footnote at the beginning of this paper.

Paper 9.25*

YIELD OF 6.8d U^{237} AT THE ST. LOUIS CYCLOTRON

By E. L. Brady, A. H. Jaffey, A. Turkevich, and H. Finston

The yield of 6.8d U^{237} in uranium irradiated with neutrons from 12 Mev deuterons on beryllium and lithium targets at the St. Louis cyclotron has been determined in two experiments.

Experiments have been performed to determine the production of U^{237} from the (n,2n) reaction on U^{238} when uranium was irradiated with fast neutrons at the Washington University cyclotron at St. Louis. A uranium-metal sample of about 1 kg was placed close to the beryllium target and irradiated for 23 days for a total of 62,000 μ a-hr of 12 Mev deuterons on the target. The uranium was backed by a very large mass of uranyl nitrate being irradiated for Pu^{239} production.¹

The metal was dissolved in HNO_3 , and a determination of the number of fissions that occurred was made by an assay of $12.8d Ba^{140}$. A sample of U^{237} was obtained by precipitating the uranium twice as sodium uranyl acetate according to the procedure of Connick et al.² Activity measurements of the U^{237} sample were made with an end-window Geiger-Mueller counter. In order to obtain the U^{237} counting rate at zero absorption, an aluminum absorption curve of the mounted sample was determined. By superposing this curve on the absorption curve obtained with a low-weight sample, the extrapolation to zero absorber was obtained. The results of this experiment indicated that one atom of U^{237} was formed for every 5.7 fissions that occurred, and it was estimated that the result was in error by not more than a factor of 3. The principal source of uncertainty was the extrapolation of the activity of the U^{237} sample to zero absorber. It is also possible that the chemical procedure did not adequately purify the uranium,

*This paper is reproduced direct from "Radiochemical Studies: The Fission Products," edited by Charles D. Coryell and Nathan Sugarman, National Nuclear Energy Series, Division IV, Volume 9, McGraw-Hill Book Company, Inc., New York, 1951. In that volume it appears as Paper 323. It is based on Report CC-920, Sept. 15, 1943, and Memorandum MUC-GTS-446, Feb. 11, 1944.

and a portion of the observed activity may have been due to fission products or to Np^{239} .

In later experiments a yield of one atom of U^{237} for every 5.8 fissions was obtained for a lithium target at the St. Louis cyclotron, and one atom for 83 fissions was obtained using a beryllium target. These results represent the average in an 85-lb stack of uranium metal placed directly in front of target but again backed by a large amount of uranyl nitrate.¹ These numbers are subject to the same errors as occurred in the earlier experiments in the calculation of the absolute disintegration rate from the observed activity. The data of these and the earlier experiments are summarized in Table 323.1.

Table 323.1 — Yield of U^{237} from Neutrons of Beryllium and Lithium Targets

Target	Yield of U^{237} , per cent of fissions	Fission rate, fissions/min/g of uranium/ μa
Be	17	
Be	1.2	3.8×10^7
Li	17	2.4×10^8

The discrepancy in the two sets of results for the beryllium target is surprisingly large. The effect of the smaller amount of neighboring metal in the first case would be to lower the yield of U^{237} relative to the number of fissions. However, the asymmetry of the primary fast-neutron distribution [those neutrons giving rise to the $(n,2n)$ reaction] would tend to make the yield of U^{237} larger. A comparison of the yield from neutrons from the beryllium target with the yield from neutrons from the lithium target is in agreement with expectation, namely, a smaller yield of the $(n,2n)$ reaction was expected for beryllium neutrons than for lithium neutrons because of the higher energy of neutrons from the latter.

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Paper 9.26*

YIELD OF 6.8d U^{237} IN PILE URANIUM

By W. Robinson, A. Turkevich, H. Finston, C. W. Stanley,
A. W. Adamson, and W. B. Leslie

The amount of 6.8d U^{237} produced by the $(n,2n)$ reaction on U^{238} has been determined for uranium in the Clinton Pile in several experiments. The apparent "fission yield" seems to be about 0.2 per cent in the uranium-metal slugs and perhaps a little lower in samples placed in the graphite moderator.

Experiments are reported here on the determination of the yield of 6.8d U^{237} in uranium metal from a graphite-metal pile. The first attempt to determine the extent of the $(n,2n)$ reaction on the U^{238} isotope in normal uranium in a pile was made by Robinson¹ with a uranium sample from the first chain-reacting pile at the Metallurgical Laboratory. The uranium was irradiated at a pile power of 50 watts for 5 hr, after which time it was separated from the fission products by ether extraction. Because of the very soft radiations and low yield of U^{237} and because of inadequate removal of UX_1 (Th^{234}) activity, it was impossible to determine the yield of U^{237} in the sample.

The yield of U^{237} in the uranium-metal slugs of the Clinton Pile was determined by Turkevich² after the metal had been irradiated in the pile for 10.9 days. After 19 days of decay it was dissolved in HNO_3 , and portions were taken for analysis. Progress of decontamination of the fission products from uranium was followed by determining the ratio of β -to- α activity in the solutions. Toward the end of the chemical operations, this ratio had fallen to about 24 from an original value of greater than 6,000 and was shown to be unchanged either by ether extraction or by sodium uranyl acetate precipitations. This constancy of the β -to- α -activity ratio indicated radiochemically pure uranium.

*This paper is reproduced direct from "Radiochemical Studies. The Fission Products," edited by Charles D. Coryell and Nathan Sugarman, National Nuclear Energy Series, Division IV, Volume 9, McGraw-Hill Book Company, Inc., New York, 1951. In that volume it appears as Paper 324. It is based on Reports CC-529, Mar. 13, 1943; CC-1331, Feb. 7, 1944; CC-1767, June 12, 1944; and CN-2833, June 16, 1945.

Six uranyl acetate precipitations, interspersed with several LaF_3 scavenging precipitations, an ether extraction, and several $\text{Fe}(\text{OH})_3$ and Nb_2O_5 scavenging precipitations at controlled pH were required. It was found that Np^{239} was the most serious contaminant, and much of the above laborious procedure could have been avoided by using special methods to remove this activity.

The final solution was evaporated on mica in samples of various thicknesses, the thinnest being about 0.2 mg/cm^2 . It was thus thin enough for both reliable β - and α -activity measurements. The former were done with standard mica-window (2.7 mg/cm^2) Geiger-Mueller tubes. The invariance of the β -to- α ratio in the later chemical operations and the decay and absorption curves of the radiations, which

Table 324.1 — Summary of Calculation of Rate of Production of U^{237} in Clinton Pile Metal

α activity of sample (geometry factor of 50 per cent), c/m	84
β activity of sample (geometry factor of 30.1 per cent, 7.6 mg/cm^2 of absorber), c/m	411
β activity corrected to 100 per cent geometry factor, c/m	1365
β activity corrected to zero absorber, ³ c/m	4040
β disintegration rate, dis/m/mg of uranium	3.73×10^4
β disintegration rate at end of irradiation (20.44 days of decay), dis/m/mg of uranium	2.98×10^5
Saturation activity, dis/m/mg of uranium	4.44×10^5
Rate of production of U^{237} , atoms/min/mg of uranium	4.44×10^5
Fission rate,* fissions/min/mg of uranium	4.1×10^7
Ratio of rate production of U^{237} to fission rate	0.011

*Determined as the saturation activity of 12.8d Ba^{140} divided by the fractional fission yield,⁴ 0.061.

agreed excellently with those of Brady and Rubinson,³ indicated that the activity isolated was 6.8d U^{237} . The β -to- α ratio, after suitable corrections, gives a basis for estimating the yield of the $(n,2n)$ reaction per gram of uranium in the sample used. These data are given in Table 324.1.

As is evident from Table 324.1, the correction to zero absorber amounted approximately to tripling the specific activity; this correction was made by extrapolating along the known absorption curves³ and by assuming that there was only one recorded particle per nuclear disintegration. The number of fissions per milligram of uranium was estimated roughly by radiochemical assay of 12.8d Ba^{140} in the original metal solution. The assay gave 2.55×10^5 disintegrations per minute (dis/m) per milligram of uranium for Ba^{140} 26.9 days

after the end of the irradiation, or a corresponding fission rate of 4.1×10^7 fissions per minute per milligram. A comparison of this value with the production of U^{237} from Table 324.1 gave a 1.1 per cent apparent fission yield for U^{237} . The term "fission yield" as used here refers to the yield of U^{237} per fission occurring in the metal.

The uncertainty in this result was realized to be due, in large measure, to the above-mentioned correction to zero absorber, but it was thought that the determination of the yield of the (n,2n) reaction per milligram of uranium was accurate to within a factor of 2. Later work⁵ on the radiations of U^{237} indicates that about half the particle radiations of U^{237} are conversion electrons; consequently the above yield should be divided by 2 to give a yield of about 0.6 per cent.

A repetition of this experiment by Finston and Turkevich⁶ with the same technique gave a result of 0.4 per cent for the fission yield of U^{237} . This value was thought to be more reliable because the exposure of the metal in the pile was monitored more satisfactorily by the activity of $12.8d Ba^{140}$ than was done previously. The result still assumed the doubtful extrapolation and interpretation of the absorption curve of U^{237} which was used earlier and, if corrected for conversion electrons,⁵ would give a yield of about 0.2 per cent. This is considered to be the most reliable estimate of the yield of U^{237} in Clinton Pile uranium.

During a study of the Szilard-Chalmers method of concentration of U^{237} , another opportunity presented itself⁷ to estimate the yield of U^{237} as 0.3 per cent of the number of fissions. The sources of the activity were samples of uranyl nitrate irradiated for 16 hr in the Clinton Pile. Purification of the samples was accomplished by three precipitations of the uranium as sodium uranyl acetate, a uranyl peroxide precipitation, an ether extraction, and two more sodium uranyl acetate precipitations.

The specific disintegration rate was obtained from the known geometry factor for β counting and from the assumption that the effect of the 6 mg/cm² of air and mica window of the Geiger-Mueller tube reduced the counting rate twofold. The fission yield of 0.3 per cent was estimated by comparing the specific activity of the U^{237} with the fission rate estimated from the neutron flux in the irradiation hole in the pile. This value should be lowered to about 0.15 to 0.2 per cent because of the effect of conversion electrons.

The quantity measured in the last experiment is not rigorously comparable to the other yields reported here, but it gives an estimate of the amount of U^{237} produced in uranyl nitrate irradiated in experimental holes in the graphite moderator, where the number of fast neutrons is expected to be lower than in the uranium metal.

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Editor's Note

In the references cited above, "this volume" refers to the volume of the National Nuclear Energy Series mentioned in the footnote at the beginning of this paper.

Paper 9.27*

DETERMINATION OF Th^{234} (UX_1) ACTIVITY (II)

By N. E. Ballou and D. N. Hume

A procedure is described for the radiochemical determination of Th^{234} (UX_1) activity in the presence of fission products. The method makes use of thorium as a carrier for its isotope UX_1 . Precipitations of thorium as the fluoride, hydroxide, iodate, and oxalate are performed to isolate UX_1 .

1. INTRODUCTION

The precipitation of thorium with HF and KF (probably as K_2ThF_6) removes Th^{234} (UX_1) from uranium and the fission products except the rare earths, zirconium, and the alkaline earths.¹⁻³ The addition of zirconium holdback carrier markedly reduces the coprecipitation of zirconium.^{2,3} Large amounts of UO_2^{++} cause some UO_2F_2 to come down with the fluoride precipitate; this is readily removed by washing the precipitate with 6M HF.

The solution of the thorium precipitate is accomplished by warming with HNO_3 and H_3BO_3 . The precipitation of $\text{Th}(\text{OH})_4$ removes the alkaline-earth contamination. Additional decontamination from all the fission products except zirconium and niobium (columbium) is brought about by the precipitation of $\text{Th}(\text{IO}_3)_4$ from a 4M HNO_3 solution.⁴ The precipitation of thorium with oxalic acid serves as an additional separation from zirconium and niobium and also converts the thorium to a weighable form.

2. PROCEDURE

Step 1. To 5 ml or less of uranium and fission-product sample in a lusteroid tube, add 1 ml of conc. HNO_3 , 20 mg of standard thorium

*This paper is reproduced direct from "Radiochemical Studies: The Fission Products," edited by Charles D. Coryell and Nathan Sugarman, National Nuclear Energy Series, Division IV, Volume 9, McGraw-Hill Book Company, Inc., New York, 1951. In that volume it appears as Paper 310. It is based on Report CN-1312, May 15, 1945.

carrier, and 10 mg of zirconium holdback carrier. Dilute to 20 ml and add 3 ml of conc. HF and 3 ml of 6M KF. Centrifuge, and wash with 5 to 10 ml of 6M HF.

Step 2. Dissolve the precipitate with 2 ml of 6 per cent H_3BO_3 and 2 ml of conc. HNO_3 (Note 1). Dilute to about 15 ml, add 5 mg of barium holdback carrier, and precipitate with 3 to 4 ml of conc. NH_4OH . Centrifuge, and wash with 20 ml of H_2O .

Step 3. Add 8 ml of conc. HNO_3 , 10 drops of 3 per cent H_2O_2 , and 20 ml of 0.35M HIO_3 to the precipitate. Cool, and let the $\text{Th}(\text{IO}_3)_4$ precipitate stand for 5 min (Note 2). Centrifuge, and wash the precipitate with 10 ml of a mixture of 3M HNO_3 and 0.03M HIO_3 .

Step 4. Dissolve the $\text{Th}(\text{IO}_3)_4$ precipitate by the addition of 2 ml of conc. HCl , dilute to about 20 ml, and pass in SO_2 until the solution becomes colorless. Add 5 ml of conc. NH_4OH and centrifuge.

Step 5. Dissolve the hydroxide precipitate in 8 ml of conc. HNO_3 , and add 5 mg of Ce(III) carrier, 0.5 ml of 3 per cent H_2O_2 , and 20 ml of 0.35M HIO_3 . Cool, and let the $\text{Th}(\text{IO}_3)_4$ precipitate stand for 5 min. Centrifuge, and wash with 10 ml of 0.035M HIO_3 . Add 2 ml of conc. HCl to the precipitate, dilute to 20 ml, and pass SO_2 into the solution until it is colorless. Precipitate $\text{Th}(\text{OH})_4$ by the addition of 5 ml of conc. NH_4OH , and centrifuge and wash the precipitate with about 20 ml of H_2O .

Step 6. Dissolve the precipitate in 1 ml of 6N HCl , add 15 ml of H_2O , heat the solution to boiling, and add 15 ml of sat. $\text{H}_2\text{C}_2\text{O}_4$. Cool the $\text{Th}(\text{C}_2\text{O}_4)_2$ precipitate in an ice bath for 10 min, and filter it on a weighed filter-paper disk. Wash with alcohol and ether, and use the same technique for drying and weighing as in the rare-earth procedures³ (Note 3). Count without excessive delay (Note 4).

Notes. 1. Additional H_3BO_3 and HNO_3 may be necessary if much lanthanum was present in the original sample.

2. Hydrogen peroxide reduces cerium to the Ce(III) state, in which it is not precipitated from strongly acid solutions by IO_3^- .

3. The precipitate is weighed as $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$. The carrier must be standardized in the same manner.

4. The thorium precipitate should not be allowed to stand very long before the activity measurements are made, since the β -active disintegration products of thorium contribute an increasingly larger fraction of the total activity with time.

3. DISCUSSION

The procedure has been tested by using carrier-free tracers of cerium, yttrium, ruthenium, strontium, zirconium, and tellurium.

The final thorium oxalate precipitate was contaminated to the extent of 0.06 per cent of the gross added tracer activity.

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Paper 9.28

GAMMA RADIATION OF U^{235} (Th^{231})

By R. L. Macklin

[Editor's Note: Contribution from the Clinton Engineer Works, Carbide and Carbon Chemicals Corporation. Based on Report K-97. Prepared for publication April 1947. Presented at the AEC Information Meeting in Chicago, Ill., on Apr. 21, 1947.]

ABSTRACT

Evidence for the existence of a gamma ray accompanying the alpha decay of U^{235} is presented. The energy of the gamma ray, as determined by several independent absorption measurements, is 162 Kev. The radiation is thought to occur with about 80 per cent of the disintegrations as indicated by alpha-ray-range measurements.

In a sample of pure uranium the three isotopes U^{234} , U^{235} , and U^{238} spontaneously emit alpha particles and are thereby transformed into the thorium isotopes Th^{230} , Th^{231} , and Th^{234} . In the case of U^{235} most of the alpha particles emitted are accompanied by a weak gamma ray of 162-Kev energy. The remainder of the U^{235} alpha rays correspondingly have 162 Kev more energy. The best information currently available gives a branching ratio of 4 to 1 for these two alpha rays from U^{235} and hence a yield of 80 gamma rays per 100 alpha disintegrations.

This gamma ray was first noticed in a product sample from the gaseous diffusion plant in April 1946.¹ By reference to the unusual history of such a sample and comparison with another sample prepared by the electromagnetic process it was possible to prove fairly conclusively that the gamma radiation accompanied the decay of U^{235} . Since the low specific activity of U^{235} and its contamination with the more active U^{234} make a direct proof of the U^{235} gamma-ray origin

by coincidence methods unlikely, it is perhaps useful to outline the methods used in 1946.

Uranium for the gaseous diffusion plant is first purified by extraction of the uranium nitrate from aqueous solution. In the next purification step the uranium, as UF_4 , is treated with gaseous fluorine, and the UF_6 formed is distilled away.

In the diffusion cascade the UF_6 gas is distilled into the system near the "bottom" (heavy-fraction end). Then it passes through or past a very large number of porous plates.

The discovery of a constant gamma activity (about 1000 c/min) in a top product sample (1 kg of UF_6 solid in a $\frac{1}{4}$ -in.-wall nickel container) superimposed on a growing UX_1 and UX_2 gamma activity (extrapolating to an additional 300 to 400 c/min at equilibrium) permitted several possible explanations.

1. A small fraction of the UX_1 (nonvolatile fluoride) passed through the porous plates of the cascade as a dust, giving rise to the observed activity.

2. The constant gamma activity was associated with the very slow alpha decay of U^{234} or U^{235} .

3. There was a gamma activity associated with the decay of UY (suggested by Booth of Columbia) whose typical growth period was masked by the decay of radon and its active deposit.

To rule out the first of these possibilities an old sample of feed material containing UX_1 and UX_2 at equilibrium was distilled through a single porous plate considerably coarser than those used in the diffusion cascade. The residual activity of the distilled material (approximately 1 kg of UF_6) was about 24 c/min and increased with the half-life period of UX_1 to about 500 c/min at equilibrium. Since the product sample contained roughly two thirds as much U^{238} , parent of UX_1 , as the feed sample, the counting rate of UX_1 and UX_2 in equilibrium with it should be about 340 c/min. Thus the initial activity of 1000 c/min should have decreased to about 340 c/min as a limit if it were due to UX_1 compounds in the sample. The observed increase to about 1300 to 1400 c/min indicates that less than 10 per cent of the equilibrium amount of UX_1 was present in the product samples. Since less than 4 per cent was present in the normal sample after a single distillation through a porous plate, it seems logical to infer that considerably less than 4 per cent remained in the product sample which passed through many more plates with considerably smaller pore size. Thus the possibility given in item 1 above was ruled out.

With the first possibility ruled out, a simple experiment to decide between the remaining two was desired. While better sample preparation and counting would unquestionably have sufficed since the UY

half life is 1 day and that of radon almost 3 days, problems of transferring enriched uranium made this undesirable. A new sample of UF_6 frozen down in a nickel container as before was drawn from a point somewhat below the top of the diffusion cascade. Since radon is swept more rapidly to the top of the cascade than UF_6 but not entirely removed with the N_2 , HF , and other very light gases in the purge cascade, it should tend to concentrate rather sharply in the top cells of the main cascade. The fresh sample drawn below should have contained only about 20 per cent as much radon (if any was present) as the sample from the top of the cascade. But this sample showed no appreciable drop in initial activity per kilogram, and hence it appears that no effective quantity of radon is present in either the top sample or that withdrawn below the top. This ruled out the third explanation previously mentioned, and it was therefore concluded that the gamma radiation observed accompanied the alpha decay of either U^{234} or U^{235} .

To determine whether the gamma rays were due to U^{234} or U^{235} , two samples of about 1 g each were obtained. One was U_3O_8 obtained from the diffusion cascade product. The other was UF_4 derived from the electromagnetic-separation-plant product. The two samples contained nearly equal percentages of U^{234} , but their U^{235} content differed by a factor of 3. Utilizing the previous experiments to evaluate the effect of UX_1 and UX_2 present, the ratio of gamma counting rates of the two samples was predicted. Under the assumption of gamma radiation from U^{234} the total-gamma-activity ratio was calculated to be 0.63. For U^{235} gamma radiation a corresponding ratio of 2.32 was derived. The ratio observed was 2.31, reproducible to 1 or 2 per cent. Thus the constant gamma activity was shown proportional to the U^{235} content of the sample.

Absorption measurements were made on the 1-g sample of UF_4 . These showed a prominent gamma-ray component at about 162 Kev.

A pair of samples from the top and bottom of the diffusion cascade was prepared, and absorption measurements with both lead and aluminum were made at K-25 and later (July 1946) at Oak Ridge National Laboratory. By subtracting the rates observed for the two samples a net counting rate proportional to a known weight of U^{235} was obtained. The 162-Kev radiation was fully confirmed (see Fig. 1). Two weaker radiations were found, corresponding to L and M x-rays. No curvature indicative of beta radiation was discerned. The intensities of these three radiations were comparable, but a reliable estimate of absolute intensity has not been available from these measurements. The absolute calibration of the counters used is being considered.

The possibility of an obscured K x-ray line of intensity comparable with that of the observed L and M x-rays has been removed by recent observations on a thin 16-mg sample of highly enriched material. The L and M lines were observed to have a very high intensity, while the 165-Kev line was less intense by a factor of about 1000. No K line was observed.

The yield of gamma rays per alpha ray from U^{235} can be estimated from K-25 counting data as being between 10 and 100 per cent, depending on the value assigned to counter efficiency at 165 Kev. A more precise estimate is available, however, from previous work with alpha-range-selecting counters. This technique has been used by Kovarik and Adams, Curtis, Frisch, and others. The work of Clark, Spencer-Palmer, and Woodward² in England with normal and enriched uranium is of particular interest. They found the usual three alpha groups and attempted quantitative measurement of each. Upon comparing their data for the activity ratio of U^{235} to U^{238} (3.60 per cent) with other determinations, particularly Nier's 4.6 per cent, they found a significant discrepancy. The alpha-particle emission rate in the 4.52-Mev group was only 79 per cent as large as the total U^{235} disintegration rate. A measurement of the U^{238} alpha rays in a slightly enriched sample showed no increase over normal. A search for a fourth alpha-ray group proved unsuccessful. The possibility of a U^{235} alpha-ray group obscured by the U^{234} rays (4.71 Mev) was considered along with the possibility of a neptunium 235 branched-chain disintegration. The gamma ray of 165 Kev since discovered indicates, of course, that there was a weaker alpha-ray group at about 4.69 Mev. An experiment to locate and record this group directly was being considered at the time of writing.

As a U^{235} detector this gamma ray is far from ideal. In the absence of anything better, however, it is being applied as a means of detecting localized accumulations of U^{235} inside equipment not conveniently amenable to direct observation.

Fig. 1 — Two lead absorption curves of U^{235} determined by difference in counting rates.

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Paper 9.29

RADIATIONS OF Pa^{232}

By A. H. Jaffey and Q. Van Winkle

[Editor's Note: Contribution from the Argonne National Laboratory. Based on Report ANL-4193. Prepared for publication Oct. 4, 1948. Preliminary calculations were reported in Report CN-3001, May 1945, pp. 19-21.]

ABSTRACT

Pa^{232} was discovered by Gofman and Seaborg,¹ who reported it to be a beta- and gamma-ray emitter with a 1.6-day half life. In the course of another experiment,² further investigation was made on Pa^{232} . From this work and other results, the half life was determined to be 1.32 days (reported elsewhere).³ Although the results of the measurements on the Pa^{232} radiations are only preliminary, they are being reported here since no further work has been done at this laboratory.

1. EXPERIMENTAL WORK

1.1 Chemical Operations. The Pa^{231} was precipitated in a quartz tube with ammonia, washed, dried at 100°C , and sealed in the tube for bombardment in the Argonne heavy-water pile. Subsequent to bombardment, the solid was dissolved, and samples were prepared on quartz plates. The Pa^{232} formed was found to be relatively free of all radiochemical contamination except that due to Pa^{231} .

1.2 Apparatus. The absorption curves described in the following paragraphs were measured with brass-walled thin-mica-window argon-alcohol filled (10 cm Hg total pressure) Geiger-Mueller counters.⁴ The circuits were of the scale-of-eight Cyclotron Specialties type with Neher-Harper quench circuits.

1.3 Experiment. Absorption curves were measured with aluminum and lead, and, after complete decay of the Pa^{232} activity, similar measurements were made on the residual activity due to Pa^{231} . This background was subtracted before correcting the absorption curves for decay during measurement. A half-life value of 1.32 days was used for these corrections. Losses at high counting rates were corrected by calibration of the Geiger-Mueller tubes through the use of the paired-source technique.

2. RESULTS

2.1 Hard Gamma Radiation. The lead absorption curve in Fig. 1 shows a gamma ray with a half thickness of 10.8 g/cm^2 . According to Heitler's curves^{5,6} relating half thickness to energy, this value should correspond to a gamma-ray energy of 1.10 Mev. It has been proposed elsewhere⁷ that the absorption method used in this experiment tends to give high values for the half thickness. In this method, the sample is placed about 5 cm from the Geiger-Mueller tube, whereas the lead absorbers are placed next to the window of the tube. As more absorbers are added, they are placed in contact with the absorber next to the window. This procedure minimizes scattering of gamma radiation around the absorbers into the Geiger-Mueller tube and also guarantees that the electrons (photoelectrons, Compton electrons and electron pairs) formed in the absorbers always have the same geometry relative to the Geiger-Mueller tube. However, the geometry at an absorber is fairly high, so that a secondary gamma ray emerging from a Compton scattering process has a relatively good chance of being detected by the Geiger-Mueller tube. Hence the counting rate falls off more slowly with addition of absorbers than it would with very low (i.e., beam) geometry, where every scattered gamma ray is scattered out of the beam. It is for the beam case that Heitler's curves are calculated, so that for given gamma-ray energies the method used here would give higher half thicknesses than does Heitler. As pointed out by Jaffey and Magnusson,⁷ the effect is even worse for absorbers of lower atomic weight. This is borne out by an aluminum absorption curve of the Pa^{232} sample; the measured half thickness (16.7 g/cm^2) corresponds (Heitler) to an energy of 1.9 Mev. An evaluation⁷ of the quantitative aspects of the discrepancies indicates that the Pa^{232} gamma-ray energy is probably between 1.0 and 1.05 Mev.

2.2. Other Quantum Radiation. X-rays. Figures 2 and 3 show lead and aluminum absorption curves, respectively, determined with the sample 3.5 cm from the Geiger-Mueller tube and with a 1.9 g/cm^2 beryllium absorber over the sample. The lead or aluminum absorbers

were placed next to the Geiger-Mueller window. The beryllium absorber was used to cut out beta particles and electrons with a minimum of x-ray absorption.

The lead absorption curve in Fig. 2, after subtraction of the hard gamma-ray component, analyzes into two components with half thicknesses of 900 and 6.8 mg/cm², respectively. The former corresponds⁶ to a gamma-ray energy of about 225 Kev, while the latter occurs in the region of the L absorption edges of lead. As a result, the answer is multivalued, and any or all of the energies⁶ 11.3, 13.2, and 19.2 Kev would correspond to the half thickness 6.8 mg/cm².

Subtraction of the hard gamma-ray component in the aluminum absorption curve (Fig. 3) leaves two components, 112 and 37 mg/cm², which correspond⁶ to the energies 16.5 and 11.3 Kev, respectively.

The low-energy components found in both the aluminum and lead absorption curves are probably L x-rays (presumably of U²³²). It has been shown elsewhere⁷ that, if a synthetic aluminum absorption curve is drawn for the five most intense components of the L x-rays, this curve can be arbitrarily analyzed into two components with half thicknesses of about 120 and 40 mg/cm², respectively. The softer components of the aluminum absorption curve evidently have this structure and hence are probably L x-rays. The component having a half thickness of 6.8 mg/cm² of lead probably corresponds to the L x-rays, which have energies of 13.6 to 20.3 Kev.⁸

The lack of agreement between the lead and aluminum absorption curves on the 225-Kev component is somewhat disturbing. It is possible that it could have been missed in the aluminum curve since this absorption curve was carried out only to 6 g/cm² of aluminum. Because of the low counting rate of the 225-Kev gamma ray (from Fig. 2, about one-seventh that of the hard gamma ray) and the large aluminum half thickness (5.85 g/cm²), it would have been quite possible to miss this component.

2.3 Beta Particles. Figure 4 shows the aluminum absorption curve for a Pa²³² sample mounted fairly close to the Geiger-Mueller tube. After subtraction of the hard gamma ray, the first component to be "peeled off" proved to have a half thickness of 78 mg/cm². The most suitable interpretation is that this component is due to the L x-rays and that the inability to get the apparent two components found in Fig. 3 is due to the insufficiency of points in this region. The value 78 mg/cm² seems to be an average of the two half thicknesses found in Fig. 3. This interpretation is further substantiated in Sec. 2.4 where abundance considerations are discussed.

The next component (Fig. 5) has an initial half thickness of about 33 mg/cm². On the assumption that it is due to another beta particle

or to a conversion electron, its range is roughly 150 mg/cm^2 , which corresponds to an energy of 480 Kev.^{9,10} It might also be an L x-ray component. However, this assumption can probably be eliminated on abundance considerations (Sec. 2.4).

The final component (Fig. 5) has an initial half thickness of 5.8 mg/cm^2 and a range of about 70 mg/cm^2 (280 Kev).^{9,10} It is, apparently, the major beta-particle constituent of Pa^{232} .

2.4 Abundance Considerations. Table 1 gives the relative abundances of the components found in Figs. 4 and 5, and Tables 2 and 3 give the relative abundances of those in Figs. 3 and 2, respectively.

The absorption in the beryllium absorber was calculated as follows:

1. The energies of the most intense components of the L x-rays of uranium⁸ are 13.6, 13.5, 17.3, 16.5, and 20.3 Kev, and their relative intensities⁸ are 100, 11, 49.4, 28, 12.

2. The relative efficiency of detection of each component was taken as being proportional to its mass-absorption coefficient⁶ in argon (the major constituent of the gas filling).

3. The beryllium absorption coefficient of each component was determined, and, using as weighting factors the relative intensities and the relative detection efficiencies, it was calculated that 0.43 of the total x-ray counts passed through the beryllium absorber. Thus x-ray counts through the beryllium absorber required correction by the factor 2.3. The value 2.3 is a lower limit since the presence of heavy-element impurities in the absorber would have resulted in greater x-ray attenuation.

The efficiencies for detection of the quantum radiation were determined as follows:

1. Jaffey and Magnusson⁷ found the detection efficiency of the L x-rays of Pu in a similar argon-filled Geiger-Mueller tube to be about 2 per cent. Since the energies of the uranium L x-rays are almost the same, the same value is used here.

2. They also found the detection efficiency of a 1.2-Mev gamma ray in the same type of Geiger-Mueller tube to be about 1.3 per cent. Since the efficiency of a Geiger-Mueller tube for gamma rays is approximately a linear function of energy in this energy region,^{11,12} the efficiency for a 1.0-Mev gamma ray may be taken to be approximately 1 per cent.

3. Studier¹³ found the efficiency of a similar Geiger-Mueller tube to be about 0.5 per cent for a 0.3-Mev gamma ray.

2.5 Summary. Although the absorption data are not sufficiently good to establish clearly the decay scheme, it seems likely that for each soft beta particle there is one hard gamma ray and one L x-ray. The data from Tables 2 and 3 indicate only one x-ray per gamma ray.

For this reason, the component with the half thickness 33 mg/cm^2 (Table 1) is probably not an x-ray but a conversion electron (or another beta particle).

The large number of L x-rays, with no indication of K x-rays, suggests that there may be a soft gamma ray (less than 100 Kev) which is almost entirely converted in the L shell. This seems to be true⁷ also of Np^{238} , which is an analogous nuclide. The resulting conversion electrons would be so soft as to be absorbed in the mica window and hence would not be detected.

A single beta particle (approximately 0.28 Mev) in coincidence with a hard gamma ray (1.0 to 1.05 Mev) and with a soft gamma ray (less than 100 Kev) almost completely converted in the L shell would explain most of the radiations. Just how a 0.48-Mev conversion electron or beta particle (5 per cent abundance) and a 0.23-Mev gamma ray (30 per cent abundance) fit in is not at all clear. Further work, including coincidence measurements, is necessary to clear up this point.

Table 1—Relative Intensities of Radiations as Taken from the Aluminum Absorption Curves in Figs. 4 and 5

Type of radiation	Radiation at zero-absorber extrapolation, c/min	Estimated counting efficiency	Radiation corrected for efficiency, c/min	Radiation, (corrected) relative to hard gamma ray, c/min
Soft beta particle	20,000	1.0	20,000	1.2
Electron (or x-ray)	820	1.0 or 0.02	820 or 41,000	0.05 or 2.6
L x-ray	520	0.02	26,000	1.6
Hard gamma ray	160	0.01	16,000	1.0

Table 2—Relative Intensities of Radiations as Taken from the Aluminum Absorption Curve of Be-Covered Sample (Fig. 3)

Type of radiation	Radiation at zero-absorber extrapolation, c/min	Estimated counting efficiency	Radiation corrected for efficiency, c/min	Radiation corrected for absorption in Be, c/min	Radiation, (corrected) relative to hard gamma ray, c/min
Hard gamma ray	735	0.01	73,500	73,500	1.0
L x-ray	675	0.02	33,750	77,625	1.05

Table 3—Relative Intensities of Radiations as Taken from
Lead Absorption Curve of Be-Covered Sample (Fig. 2)

Type of radiation	Radiation at zero-absorber extrapolation, c/min	Estimated counting efficiency	Radiation corrected for efficiency, c/min	Radiation corrected for absorption in Be, c/min	Radiation (corrected) relative to hard gamma ray, c/min
Hard gamma ray	740	0.01	74,000	74,000	1.0
Soft gamma ray	112	0.005	22,400	22,400	0.3
L x-ray	555	0.02	27,750	63,800	0.85

Fig. 1—Lead absorption curve for Pa^{232} obtained with the sample mounted 5 cm from the Geiger-Mueller tube.

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Fig. 2—Lead absorption curve for Pa^{232} determined with the sample mounted 3.5 cm from the Geiger-Mueller tube and with a beryllium absorber (1.9 g/cm²) over the sample.

Fig. 3—Aluminum absorption curve for Pa^{232} obtained with the sample mounted 3.5 cm from the Geiger-Mueller tube and with a beryllium absorber (1.9 g/cm^2) over the sample.

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Fig. 4—Aluminum absorption curve for a Pa^{232} sample mounted on quartz 1.0 cm from the Geiger-Mueller tube (mica-window half thickness, 2.77 mg/cm^2).

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Fig. 5—Aluminum absorption curve for a Pa^{232} sample mounted on quartz 1.0 cm from the Geiger Mueller tube (mica-window half thickness, 2.77 mg/cm²; mica plus air absorption, 3.94 mg/cm²).

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Paper 9.30

REPORT ON RADIATIONS OF UY

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1. INTRODUCTION

In the course of a cross-section measurement¹ on the $\text{Th}^{230}(\text{n}, \gamma)\text{Th}^{231}$ reaction by direct determination of the Th^{231} (or UY) disintegration rate, it was found necessary to have some information on the UY decay scheme. Such information was necessary in order to evaluate the fraction of the counts measured which were due to disintegration beta particles. Some preliminary work has been done on the decay scheme by the use of absorption methods. The poor resolution of these methods enabled the determination of only the gross features of a decay scheme, which were sufficient for the purposes of evaluating disintegration rates (with the aid of suitable corrections). The results obtained here indicate that further work is necessary to determine the correct scheme.

As indicated above, UY can be made through the absorption of neutrons by ionium, or it can be isolated from uranium samples since it is the daughter of U^{235} decay ($\text{U}^{235} \xrightarrow{\alpha} \text{Th}^{231}$). Prior to World War II the usual source of UY was natural uranium. By separating the thorium fraction from a large amount of uranium, it is possible to get a reasonable amount of UY.

Unfortunately, UY so separated always has large amounts of UX_1 (Th^{234}) and UX_2 present, even when short periods (1 to 2 days) of growth are used in order to increase the relative concentration of the short-lived (25.6 hr) UY over that of the 24.1-day UX_1 . Most measurements made on UY separated from natural uranium were made by difference.

The UX radiation was measured after the decay of the UY, and, after correcting for the UX_1 decay, these measurements were subtracted from the measurement on the original UX + UY radiations. [UX refers to the combination of UX_1 and its short-lived descendant UX_2 (Pa^{234}).]

Because of the difficulties in such measurements, most of the work²⁻⁵ prior to the war gave incomplete results. A soft component was found, although the observed aluminum half thicknesses varied considerably [3.2 mg/cm² (Erchova); 6.2 mg/cm² (Antonoff); 6.2 mg/cm² (Kirsch); and 7.6 mg/cm² (Nishina)]. Erchova also found a harder component with a 35 mg/cm² half thickness, while Antonoff found a very soft component (0.75 mg/cm² half thickness) which he ascribed to alpha radiation.

With the availability of sources of concentrated U^{235} , it became possible to isolate UY samples with much smaller amounts of UX contamination. Such samples have been studied⁶⁻⁸ at this laboratory and by Knight and Macklin. Measurements reported early from this laboratory⁷ on a UY preparation separated from uranium containing 65 per cent U^{235} showed the presence of a number of radiations, including a soft beta of 5.6 mg/cm² aluminum half thickness, L x-rays with half thicknesses ranging from 40 to 120 mg/cm² aluminum, and a very soft radiation with a half thickness of about 1.4 mg/cm² aluminum. The abundance of the very soft radiation was almost twice that of the beta-particle component. In addition to the L x-rays, a harder quantum was found, for which the data were too poor to determine the energy, although it was suspected that it might be a K x-ray. The quantum radiations were proved to be such by measurement through sufficient beryllium absorber to cut out all beta particles. Several suggestions were made for possible decay schemes.

Knight and Macklin⁶ found the soft beta particle and determined a value of 7.0 mg/cm² for the aluminum half thickness. In addition, they found two more components with half thicknesses of 820 and 104 mg/cm², respectively, which they ascribed to a 34-Kev gamma ray and to a 16-Kev L x-ray. Knight and Macklin suggested a decay scheme involving a beta decay (7 mg/cm² component) followed by a 34-Kev gamma, which was highly converted, thus giving rise to L x-rays. They ascribed the very soft component found in this laboratory to a mixture of conversion electrons and M x-rays.

More recent investigation in this laboratory has shown that this decay scheme is probably incomplete. The work described in this paper summarizes both the earlier experiments and the more recent measurements. Since both the results described here and those of Knight and Macklin suggest a single beta particle followed by a num-

ber of other radiations (conversion electrons, x-rays, and gamma rays), the determination of the true disintegration rate from the counting rate is probably not seriously affected by the details of the disintegration scheme.

2. CHEMICAL SEPARATION PROCEDURE

The enriched uranium sample used contained about 95 per cent U^{235} by weight, which meant that the U^{235}/U^{238} activity ratio was approximately 100. Since, at equilibrium, the UY/UX activity ratio would be the same, a thorium sample directly separated from the uranium could have been used. However, to ensure that the UX activity would not seriously interfere even after the sample had decayed somewhat, the thorium fraction was completely separated, the uranium was purified, and the daughters were allowed to grow in for 1 or 2 days. The thorium daughters were then separated from the uranium; the resulting UY/UX activity ratio was increased by a factor of 12 to 15 over the equilibrium value.

In the first purification of the uranium, the thorium fraction was removed by precipitation with a LaF_3 carrier, after which the uranium was separated from the fluoride ion by precipitation as the hydroxide and further purified by a hexone (methyl isobutyl ketone) extraction from 10M ammonium nitrate. Following the growth period, the thorium daughters were separated by precipitation with LaF_3 carrier. To complete the separation from uranium, two more purification cycles were used, involving precipitations with zirconium iodate and LaF_3 carriers. Following the solution of the LaF_3 , the activity was separated from the lanthanum salt by extracting the thorium activity with thenoyl trifluoroacetone (TTA) in benzene solution. The nitric acid extract from the TTA contained essentially carrier-free UY, and the samples were prepared from this solution.

3. MEASUREMENTS

The results are summarized in Table 1. The best value for the aluminum half thickness of the soft beta component is about 6.1 mg/cm². According to the data summarized by Libby⁹ this corresponds to an energy of 0.20 Mev. The results obtained here also indicate that the harder radiations are due to L x-rays and several gamma rays.

An aluminum absorption curve gave two components with half thicknesses 47 and 108 mg/cm², respectively, which correspond to 12.3 Kev and 16.3 Kev, respectively. These energies are in the region of the Pa L x-rays, which could be excited if a gamma ray following the beta decay were internally converted. Although the L x-rays of

Pa range from 13 to 20 Kev, an aluminum absorption curve of the mixture of components can be (somewhat arbitrarily) "resolved" into two components, as shown in the case of Np^{238} decay by Jaffey and Magnusson.¹⁰ Thus the identification of these two components with L x-rays arising in UY decay seems reasonable. In addition to the L x-rays, the aluminum absorption curve showed a component with a half thickness of about 800 mg/cm^2 (34 Kev). All these components were proved to be quantum radiations by measuring them in a magnetic field strong enough to bend away all electrons and also by measuring them through a beryllium absorber sufficiently thick to absorb all emitted electrons (1900 and 235 mg/cm^2).

Lead absorption curves showed components with half thicknesses of 4.5 and 40 mg/cm^2 , which were shown to be quantum radiations by bending away electrons with a magnetic field. Since the first value lies in the midst of the lead L absorption edges, the 4.5 mg/cm^2 component could correspond to 9.6, 13.4, or 16.5 Kev. Evidently, this is the L x-ray observed in the aluminum curve. The harder component corresponds to an energy of 38 Kev, which checks fairly well with the results of the aluminum absorption curve. Silver and copper absorption curves similarly showed L x-rays and a gamma ray whose energy is either 34 or 38 Kev.

In addition to these components, harder quantum radiations of lower intensity were apparent in the absorption curves determined with aluminum, lead, silver, and copper. Agreement on energy values was quite poor, but it seemed fairly certain that there was a gamma ray with an energy lying between 60 and 70 Kev and one with an energy at or above 100 Kev which could possibly be ascribed to a K x-ray.

A soft component was observed in a low-absorption counter¹¹ with a half thickness (aluminum) of 0.9 to 1.0 mg/cm^2 and an abundance about twice that of the 6.1 mg/cm^2 component. The same radiation was also observed in absorption curves obtained with ordinary mica-window Geiger-Mueller tubes with fairly thin windows. When a beryllium absorber or a magnetic field was used to remove electrons, the half thickness increased to about 1.25 mg/cm^2 . It is possible, then, that the 0.9 mg/cm^2 component represents a mixture of soft conversion electrons and M x-rays.

For x-rays, a 1.25 mg/cm^2 half thickness may be due to a 1.3-Kev or a 3.4-Kev x-ray (multivalued because of the K absorption edge of aluminum). The x-rays from the Pa^{231} daughter of UY range from 2.4 to 4.9 Kev, which is consistent with these results, considering the experimental error in the half-thickness measurements. If the soft conversion electrons were 0.5 to 0.7 mg/cm^2 in half thickness, their energy would lie⁹ between 45 and 55 Kev. If these electrons were due

to conversion in the L shell, the converted gamma ray would have an energy of approximately 60 to 70 Kev (16 Kev taken as average Pa binding energy in the L shell), which apparently checks with the observation of a low-intensity gamma ray of about this energy. If the soft electrons had been due to conversion of the 35-Kev gamma, as suggested by Knight and Macklin,⁸ their energy would have been about 20 Kev, which corresponds⁹ to an aluminum half thickness of about 0.15 mg/cm². No such component was observed in the low-absorption counter (minimum absorption 0.3 mg/cm²).

It is further unlikely that the large number of conversion electrons observed were due to conversion of the 35-Kev gamma ray since, after correcting for counting efficiencies, the abundances of the L x-rays and the gamma ray seemed to be equal (Table 1). The ratio (at zero absorber) of the L x-ray counts to the counts due to the 35-Kev gamma ray was found to be approximately 10. Taking the average energy of the L x-ray to be 16 Kev, the half thickness in argon of this radiation would be 42 mg/cm², while the corresponding half thickness for a 35-Kev gamma ray is 380 mg/cm². For low-energy quanta, most of the counts in a Geiger-Mueller tube are those arising from absorption of the quanta in the gas of the tube; thus at low efficiencies the counting efficiency for a given type of such radiation is inversely proportional to the half thickness for absorption in the gas. Neglecting the small effect due to the alcohol, the absorption of a 16-Kev x-ray in an ordinary argon-alcohol filled Geiger-Mueller tube relative to the absorption of a 35-Kev gamma ray would be $380/42 = 9.0$. The agreement between this value and the ratio of observed counts suggests that the number of L x-rays and 35-Kev gamma rays is approximately the same, with a relatively small percentage (if any) of conversion of the gamma ray.

It also seems likely that the number of beta particles is about equal to the number of L x-rays emitted (Table 1). Using an argon-alcohol-filled Geiger-Mueller tube, the ratio of the 6.1 mg/cm² (beta) component counts (at zero absorber) to the x-ray counts was found to be about 30. If it is assumed that the number of L x-rays is approximately equal to the number of beta rays, the efficiency for counting the L x-rays of Pa is found to be about 3 per cent. This value is not unreasonable, since Jaffey and Magnusson¹⁰ found a value of 2 to 2.5 per cent for the L x-rays of Pu from the decay of Np²³⁸. [Since the L x-rays of Pa are lower in energy than those of Pu, the absorption coefficient in argon of the former would be greater, and hence the counting efficiency would be higher.]

As mentioned above, the very soft component may be a mixture of soft conversion electrons and M x-rays. The absorption coefficients

of the M x-rays in argon are quite large; thus their counting efficiency is high. It is fairly reasonable to assume, then, that somewhat less than half of the soft component counts are due to M x-rays, and the remainder of the counts are due to conversion electrons.

Some coincidence measurements were made, but they proved relatively little because of the very low counting efficiencies for the soft gamma rays involved. In these measurements, two Geiger-Mueller tubes were used with a permanently fixed absorber over one, and coincidences were measured as a function of the aluminum absorber thickness in front of the other tube. In one measurement, 475 mg/cm² of beryllium was used as the permanently placed absorber; in another, 1000 mg/cm² of aluminum was used. The former cut out electrons but allowed the L x-rays and gammas through; the latter cut out L x-rays as well as electrons. The results showed that the 6.1 mg/cm² component and the L x-rays were in coincidence with radiation that could penetrate 475 mg/cm² of beryllium or 1000 mg/cm² of aluminum; i.e., the beta particle and L x-rays were in coincidence with some gamma rays.

The half life of UY was measured using a thin-walled glass Geiger-Mueller tube: This type of tube has been found to have more reproducible characteristics than the mica-window tubes available. The tube was frequently checked with a standard, and most of the counts were within the expected statistical deviation of 0.3 per cent. Because this glass tube had a minimum absorption of about 30 mg/cm², it attenuated the UY beta radiation by almost five half thicknesses (a factor of about 30). As a result, the hard radiation of UX₂ was found to give a long-lived tail in the decay curve. Although the UX₂ concentration was quite a small fraction of the total activity, the severe attenuation of the UY beta rays made the UX radiation (which was only partially attenuated) a sizable part of the total counts measured.

A better decay curve was determined by using 1230 mg/cm² of beryllium to cut out all beta rays. Under these conditions only the quanta emitted in the UY decay were measured, although a nondecaying residuum of several counts was found after the UY decayed out. This was ascribed to incomplete separation of U²³⁵ and U²³⁴, both of which emit quantum radiation.¹²⁻¹⁵ The resolution losses were determined by using the paired-source technique¹⁶ and were found to be 0.42 per cent per 1000 c/min. Two separate preparations of UY were made from the U²³⁵ sample. Sample 1 (initial counting rate about 700 c/min) was counted down to background (about six half lives). Sample 2 (initial counting rate about 3600 c/min) was also counted down to background (about eight half lives). The half lives were calculated using a least-squares method; sample 1 gave a value 25.56 ± 0.06 hr, and

sample 2 gave 25.73 ± 0.06 hr. (The deviations represent the standard deviation calculated from the dispersion of the data.) The results probably justify a half-life value of $25.6_4 \pm 0.1$ hr.

4. SUMMARY

The results described indicate that the following components are probably present with approximately equal intensity (within perhaps 25 per cent): 0.20-Mev beta rays, L x-rays, M x-rays, 50-Kev conversion electrons, and 35-Kev gamma rays. In addition there seems to be evidence for the existence of a highly converted gamma ray in the range 60 to 70 Kev and of a low-intensity gamma with an energy of 100 Kev or greater. Despite the scanty evidence, it may be possible to combine these data into a consistent decay scheme. A tentative scheme is suggested in Fig. 1. Associated with the conversion are L and M x-rays and conversion electrons. The order of the two softer gamma rays is, of course, uncertain.

At zero absorber, using argon-alcohol-filled mica-window Geiger-Mueller tube (Table 1), the very soft component (presumably M x-rays and conversion electrons) had almost twice as many counts as the beta-ray component. The counting rate of the L x-rays was about one-thirtieth that of the beta rays, the 35-Kev counting rate was about one-tenth that of the L x-rays, while the counting rates of the other gamma rays were somewhat lower yet.

The half life of UY was measured as $25.6_4 \pm 0.1$ hr.

Table 1 — Radiations of UY

Probable type of radiation	Aluminum half thickness, mg/cm ²	Energy	Relative radiation at zero absorber, c/min	Approx. relative abundance
Mixture of M x-rays and conversion electrons	~1	2.5 to 5 Kev ~50 Kev	~2	~2
Beta rays	6.1	0.20 Mev	1.0	1.0
L x-ray	47 108	12.3 Kev 16.3 Kev	0.03	1
Gamma ray	800	35 Kev	0.003	1
Gamma ray		60 to 70 Kev	Small	
Gamma ray		100 Kev or greater	Small

Fig. 1—Decay scheme of UY.

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Paper 9.31

UPPER LIMIT TO ABSORPTION CROSS SECTION OF U^{236}

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ABSTRACT

A sample of uranium containing 1.32×10^{-4} atom % of U^{236} was exposed for about 7 days to a flux of 8.2×10^9 neutrons/sec/cm² in the thermal column of the Argonne heavy-water pile. No U^{237} above that produced in a blank sample has been detected. This indicates a maximum absorption cross section of about 30 barns for U^{236} .

1. INTRODUCTION

The isotope U^{236} is formed to the extent of about 15 per cent of the plutonium yield in thermal piles, and yet its nuclear characteristics are still largely undefined. Attempts have been made to determine its half life and radiations, but, except for reasonable certainty that it is an alpha emitter of long (10^7 to 10^8 years) half life, the search has been unsuccessful. Likewise the absorption properties for thermal neutrons are of interest. Because of this, an attempt was made to determine the cross section for the (n, γ) process on U^{236} . The sample used had a very low concentration of U^{236} , but it was felt that even an upper limit to this cross section would be of value, at least until more accurate determinations could be made as richer samples became available.

The results of a preliminary experiment of the type to be described here were announced sometime ago (Report CS-2420); an upper limit of 150 barns was set on the thermal-neutron absorption cross section of U^{236} . This experiment has been repeated here more carefully, and it is now felt that 30 barns is a reasonably safe upper limit.

The experiment consisted in counting the beta rays of the 6.83-day U^{237} which should be formed on absorption of a thermal neutron by U^{236} . The procedure was complicated by the following conditions:

1. The extremely low concentration of U^{236} present in the sample of uranium available (1.32×10^{-4} atom %). This made it imperative to increase the sensitivity of the experiment by counting infinitely thick samples of U_3O_8 .
2. The formation of U^{237} by $(n,2n)$ on U^{238} with fast neutrons. This made it necessary to work far out in the thermal column of the Argonne heavy-water pile to reduce the number of fast neutrons, with resultant loss of thermal-neutron flux. In spite of the precautions taken, the $(n,2n)$ reaction caused by neutrons arising from fissions in the sample itself caused a background effect which had to be determined and which actually limited the sensitivity of the experiment.
3. The counting of thick samples necessitated working out a procedure involving cleaning out the UX before counting and even then correcting for the UX and UY which grew in before counting.
4. The soft beta radiations of U^{237} . It has long been suspected that there are conversion electrons besides the primary beta rays in the disintegration of this nucleus. Coincidence work¹ has established this. The decay scheme appears to be too complicated to be analyzed, but it has been estimated from Engelkemeir's data that the count from a very thin sample through about 5 mg total absorber approximates (aside from geometry) the number of disintegrations. This figure could easily be in error by 50 per cent.

2. EXPERIMENTAL PRELIMINARIES

A technique of mounting and counting U_3O_8 samples was developed and standardized for this experiment. The uranium was cleaned of disintegration products by several sodium uranyl acetate precipitations and then was brought down several times with H_2O_2 and ignited to U_3O_8 . Standard 33-mil aluminum mounting cards were made with a well in the center (2 cm in diameter and 16 mil deep). About 100 mg of the U_3O_8 was weighed out into these, slurried up evenly with a few drops of water containing a little aerosol, and baked dry under a heat lamp. The powder was finally bound with a little collodion solution (about 0.2 mg/cm²). The samples were counted on the top shelf of the standard mica-window Geiger-Mueller counter. The total absorber consisted of cellophane, 3.3 mg/cm²; air, 0.6 mg/cm²; and mica window, 4.3 mg/cm². The "geometry factor" was about 26 per cent. The reproducibility of this mounting technique was tested with UX radiations and found adequate (within a few per cent either way).

Usually about 4 hr passed after the UX + UY cleanup before the samples were counted. Because of the size of the samples, they had thus acquired of the order of 200 to 300 counts/min before counting. Although most of this was hard UX₂ beta rays, an important portion (a few hours after cleanup) was due to UY (daughter of U²³⁵) which, because of its 24.5-hour half life, grows in much more rapidly than UX₁. UY has a weak beta ray with a half thickness of about 6.8 mg/cm². A top-shelf aluminum absorption curve on a normal 114-mg U₃O₈ sample which had been treated in the standard fashion is shown in Fig. 1. It was obtained 3 hr after cleanup. The ratio of counts through zero added absorber to that through 139 mg/cm² aluminum is about 2.6. This ratio gradually falls to about 2.1 after the UY begins to saturate and the UX₁ grows in (about 1 day).

Besides conversion electrons, 6.83-day U²³⁷ has a main beta ray of about 7 mg/cm² half thickness.² The count through 134 mg/cm² is but a few per cent of the count through zero added absorber. An absorption curve of a sample of about 100 mg of U₃O₈ containing appreciable amounts of U²³⁷ and cleaned up and mounted in the standard fashion is shown in Fig. 2. It is evident that the count through 139 mg/cm² aluminum may be used as a measure of the UX + UY correction to the U²³⁷ count at zero absorber.

Making the UX-UY corrections in the above indicated manner, the counting yield of the thick samples for U²³⁷ beta rays was determined by counting samples of U₃O₈ of various sizes containing known amounts of U²³⁷. The counts were referred to the U²³⁷ count present in a thin (0.0375 mg/cm²) sample of U₃O₈ mounted on mica and counted without cellophane on the top shelf of the counters. The "effective counting weight" of a thick sample is the counts per minute divided by the counts per minute per milligram of a thin sample, and it is plotted in Fig. 3 as a function of sample weight. It is evident that above 90 mg of U₃O₈ the count of U²³⁷ is independent of weight and equivalent to 19.0 mg of a thin sample. All samples counted in the cross-section determination contained between 95 and 115 mg U₃O₈. As indicated in Sec. 1, the counts per minute of the thin sample divided by the geometry (0.258) is identified with the disintegrations of U²³⁷ per minute.

The uranium sample enriched in U²³⁸ came from a slug X-11 which had undergone a 2.06×10^6 kw-hr bombardment at Oak Ridge National Laboratory, extending over 123 days and ending Apr. 8, 1944. The U²³⁷ from the (n,2n) reaction was allowed to decay, and decontamination from fission products was accomplished by ether extractions, specific decontaminations, sodium uranyl acetate precipitations, and pre-precipitations with Superoxol. The specific decontaminations consisted of

precipitations of uranium in the presence of holdback carriers. It was shown that the standard procedure reduced the beta activity of this sample as low as it did normal unirradiated uranium.

The concentration of U^{236} in this sample was determined in the following manner.

By an analysis made at Oak Ridge National Laboratory, it was determined that the bombarded metal contained 5.7×10^{-6} g of plutonium per gram of uranium, or 1.43×10^{16} atoms of plutonium per gram of uranium. Since the ratio of captures in U^{238} to fissions in thermal piles is 0.88, this means that, during the course of production of plutonium, the number of U^{235} atoms (per gram of uranium) undergoing fission was

$$\frac{1.43 \times 10^{16}}{0.88} = 1.63 \times 10^{16}$$

Since 0.17 of the neutron absorptions by U^{235} results in the formation of U^{236} by neutron capture, the number of U^{236} atoms (per gram of uranium) formed by capture is

$$1.63 \times 10^{16} \times \frac{0.17}{0.83} = 3.34 \times 10^{15}$$

The number of atoms per milligram of uranium is 3.34×10^{12} .

$$\text{Atomic } \% U^{236} = \frac{3.34 \times 10^{12} \times 10^3 \times 238 \times 100}{6.02 \times 10^{23}} = 1.32 \times 10^{-4}$$

3. EXPERIMENTAL PROCEDURE

The irradiated uranium was prepared as U_3O_8 ; 1 g was weighed out, dissolved in HNO_3 , evaporated to dryness, dissolved in 5 cc of D_2O (to minimize reactions produced by neutrons from fissions in the sample), and sealed in a quartz tube. A sample of ordinary uranium was identically prepared to be used as a blank for the U^{237} to be derived from the $(n,2n)$ reaction on U^{238} . The samples were labeled and placed 3 in. apart on the axis of the thermal column of the Argonne heavy-water pile. They were 64 cm from the tank. The samples were given an irregular 7-day bombardment (a log of the bombardment was kept) ending at 17:11 on Mar. 10, 1945. After the irradiation, aliquots of the samples were reserved for flux determination by analysis for 12.8-day Ba^{140} known to be formed in U^{235} fission with a yield of 6 per cent.³ The remainder of each sample was freed of fission products by ether extractions, separation of specific fission products,

sodium uranyl acetate precipitations, and precipitations with Superoxol. The samples were shown to be free of fission products by invariance of the beta/alpha ratio to chemical operations known to remove various fission products. At the end of the chemical operation, a small amount of a weak beta ray of the same half thickness as U^{237} was still evident in the absorption curve of the radiations. This must be U^{237} since all fission products having beta rays of similar energy were removed by specific decontamination procedures.

The U^{237} samples, now freed of fission products, were recleaned of UX by sodium uranyl acetate and Superoxol precipitations and mounted in the standard fashion described above. They were counted without added absorber and through 139 mg/cm² aluminum absorber to correct for the contribution of uranium decay products. This procedure was repeated at intervals of about 2 days in order to follow the decay of the U^{237} .

4. EXPERIMENTAL RESULTS

Table 1 gives the results for the sample containing U^{236} (sample 1) and the blank (sample 3). Indicated are the total counts with and without added absorber and the net U^{237} count. Even at the start the U^{237} was only about 50 per cent of about 200 c/min gross, and there is no (experimentally established) difference between the two samples. The decay curves of the two samples are shown in Fig. 4. Although the points fluctuate badly (especially at the end), mainly owing to the low counts, they show some trend about a 7-day decay. It is concluded that this activity is U^{237} produced by fast neutrons since it is the same in the two samples.

The flux to which the samples were exposed was determined by radiochemical analysis of aliquots of the samples for 12.5-day Ba^{140} . From the uranium concentration, the thermal-neutron fission cross section, the fission yield of Ba^{140} (6.1 per cent), and from the log of the bombardment (fraction of saturation was 0.273), the flux was calculated in standard fashion. It came out to be the same (8.24×10^8 neutrons/min/cm²) for the two samples.

As the data indicate, there is no difference between the blank and the uranium containing U^{236} within experimental error. The writers feel that 80 c/min excess of U^{237} at the end of bombardment could have been detected. Assuming this value, the calculation may be made to convert this to an absorption cross section of U^{236} . It is believed that this cross section is less than 30 barns with an uncertainty of possibly 100 per cent due to the insensitivity of this experiment and the uncertainty in the nature of the radiations of U^{237} . The calculation follows:

With the assumed activity due to U^{237} formed by neutron capture by U^{236} at end of bombardment (through 5 mg/cm² total absorber) as 80 c/min, the value corrected to 1.0 mg of uranium [$1/(19.0 \times 0.849)$] is 5.0 c/min. [This is taken to be numerically equal to the number of disintegrations in the sample (see Secs. 1 and 2).] The activity corrected for geometry (1/0.258) is 19.4 dis/min. Calculated from the log of the bombardment, A_{237}^{∞} (fraction of sat. = 0.3908) is 50 dis/min.

$$\frac{A_{Ba}^{\infty}}{A_{237}^{\infty}} = \frac{N_{235} \times \sigma(\text{fiss}) \times Y_{Ba}}{N_{236} \times \sigma_{236}}$$

$$\sigma_{236} = \frac{N_U \times \sigma(\text{fiss}) \times Y_{Ba} \times A_{237}^{\infty}}{N_{236} \times A_{Ba}^{\infty}}$$

$$\sigma_{236} = \frac{2.53 \times 10^{18} \times 3.9 \times 0.061 \times 50}{3.34 \times 10^{12} \times 2.96 \times 10^5} = 31 \text{ barns}$$

where A_{237}^{∞} = disintegration rate of U^{237} in the sample after an infinite bombardment at standard pile power

A_{Ba}^{∞} = disintegration rate of 12.8-day Ba^{140} in the sample after an infinite bombardment at standard pile power

N_{235} = number of atoms of U^{235} in sample

N_{236} = number of atoms of U^{236} in sample

$\sigma(\text{fiss})$ = thermal-neutron fission cross section of U^{235}

σ_{236} = thermal-neutron capture cross section of U^{236}

Table 1—Counting Data on Samples Taken About 4 Hr after UX + UY Cleanup

Sample 1 (U^{236})							
Date (1945)	Time	Wt. of U_3O_8 , mg	Count through zero absorber, c/min	Count through 139 mg/cm^2 Al, c/min	U^{237} , * c/min	A-1† stand- ard	U^{237} corrected (A-1 = 3700), c/min
3/14	19:00	99.9	216	33	130	4087	118
3/16	15:20	106.1	223	55	80	3727	80
3/19	16:05	109.9	169	45	52	3532	55
3/20	01:40					3726	
3/21	15:50	114.1	205	59	51	3770	50
3/25	22:25	115.1	209	83	(-7)	3783	(-7)
3/27	14:10	114.5	183	58	32	3804	31
3/29	13:55	112.6	154	40	50	3612	51
Sample 3 (ordinary uranium)							
3/14	19:00	97.1	199	37	102		93
3/16	15:20	110.8	211	60	55		55
3/19	16:05	108.5	182	47	60		63
3/20	01:40	113.7	218	68	41		41
3/21	15:50	113.6	225	60	69		68
3/25	22:25	114.4	215	71	30		29
3/27	14:10	115.0	174	55	31		30
3/29	13:55	112.7	154	50	24		25

*The factor $1/0.384$ was used to correct the count through 139 mg/cm^2 aluminum to the UX + UY contribution at zero absorber.

†The A-1 standard was used to correct for variation in counting efficiency of Geiger-Mueller tubes.

Fig. 1 — Absorption in aluminum of radiations from an infinitely thick sample (114 mg) of U_3O_8 ; 3 hr after cleanup.

Fig. 2—Absorption in aluminum of radiations from an infinitely thick sample (~ 100 mg) of U_3O_8 containing U^{237} .

Fig. 3—Effective counting weight of U^{237} in thick samples of U_3O_8 .

719 Fig. 4 — U^{237} decay.

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