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Artificial Chains Collateral to the Heavy Radioactive Families*

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A number of heavy alpha-particle emitting nuclides, members of decay chains which are "collateral" to the heavy radioactive series, have been observed and their radioactive properties characterized. Some of these undergo branching decay by orbital electron capture. The parent isotopes are produced in bombardments of thorium with high energy deuterons or helium ions in the 184-inch cyclotron. Chemical identification has been made in all cases where needed, and the alpha-particle energies have been measured through the use of an alpha-pulse analyzer apparatus. The following are the collateral series which have been studied: $Pa^{226} \rightarrow Ac^{222} \rightarrow Fr^{218} \rightarrow At^{214}$ ($4n+2$ mass type); $Pa^{227} \rightarrow Ac^{223} \rightarrow Fr^{219} \rightarrow At^{215}$ ($4n+3$); $Pa^{228} \rightarrow Ac^{224} \rightarrow Fr^{220} \rightarrow At^{216}$ ($4n$); $U^{228} \rightarrow Th^{224} \rightarrow Ra^{220} \rightarrow Em^{216}$ ($4n$); $U^{229} \rightarrow Th^{223} \rightarrow Ra^{221} \rightarrow Em^{217}$ ($4n+1$).

I. INTRODUCTION

THE high energy particles produced in the 184-inch cyclotron make it possible to prepare and study the radioactive properties of many new nuclides with mass numbers on the neutron deficient side of beta-stability. The neutron deficient isotopes of the heaviest elements are unstable toward decay by alpha-particle emission as well as decay by orbital electron capture. Since one of the areas of interest in this laboratory is the study of the radioactive properties of the isotopes of the heaviest elements, and in particular the systematics of the alpha-decay properties, the preparation and characterization of such nuclides has been undertaken.

The present paper describes in some detail the experimental work connected with the identification and measurement of the radioactive properties of 18 new alpha-particle emitting nuclear species. These are distributed among five decay chains which can be referred to as "collateral" to the four heavy radioactive series. The five collateral chains include representatives of each of the four mass number types and hence include series collateral to each of the natural radioactive families, the uranium ($4n+2$), thorium ($4n$), and actinium ($4n+3$) families, and the synthetic neptunium ($4n+1$) family.[1–4]

The data concerning these collateral chains were published previously in summary form[5–7] with very little discussion of the experimental evidence. The present publication presents a documentation of the experimental evidence, including a number of curves which are important in this connection. It should be stated that the data reported here were taken during 1948–1949. Consequently, the energy determinations for the alpha-particles were made with instruments of poorer resolution than those available at the present time. Thus, the energies are less accurate than it would be possible to attain if the entire research were repeated; but this is not contemplated in the present program of the laboratory.

II. PROCEDURE

For the most part in these bombardments, target setups were used which would give a maximum yield of the reaction product for the target material used. Thorium metal foil was bombarded as an internal probe target in the 184-inch cyclotron to produce the four longer-lived series. The time required to dissolve the thorium metal is too long for work with half-lives of the order of two minutes, however, and in these cases thorium nitrate was used as the target material. To further reduce the time between bombardment and counting, use was made of the "jiffy" probe in the 184-inch cyclotron. With it targets were bombarded through the window of a probe tube inserted into the tank of the cyclotron and at the end of bombardment were blown quickly out of the tube by means of compressed air.

After bombardment, the thorium was dissolved in concentrated nitric acid with a small amount of ammonium fluosilicate added to catalyze the reaction, the solution made $6N$ in acid, and a protactinium or uranium fraction separated by one of several chemical procedures,[8] depending on the half-life of the desired isotope and the purification required. The protactinium or uranium parent controls the decay of the other members of the chain which quickly grow into equilibrium with it after the chemical isolation. The alpha-particle decay of these fractions after chemical separation was measured by the use of both standard alpha-particle counting devices and a 48-channel alpha-particle pulse analyzer[9]

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[1] English, Cranshaw, Demers, Harvey, Hincks, Jelley, and May, Phys. Rev. **72**, 253 (1947).

[2] Hagemann, Katzin, Studier, Ghiorso, and Seaborg, Phys. Rev. **72**, 252 (1947).

[3] Hagemann, Katzin, Studier, Seaborg, and Ghiorso, Phys. Rev. **79**, 435 (1950).

[4] For summary on neptunium family, see, e.g., G. T. Seaborg, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, *The Transuranium Elements: Research Papers*, Paper No. 22.3 (McGraw-Hill Book Company, Inc., New York, 1949); Chem. Eng. News **26**, 1902 (1948).

[5] Ghiorso, Meinke, and Seaborg, Phys. Rev. **74**, 695 (1948).

[6] Meinke, Ghiorso, and Seaborg, Phys. Rev. **75**, 314 (1949).

[7] G. T. Seaborg and I. Perlman, Revs. Modern Phys. **20**, 585 (1948).

[8] W. W. Meinke, U. S. Atomic Energy Commission Declassified Documents AECD-2738 and AECD-2750 (August, 1949).

[9] Ghiorso, Jaffey, Robinson, and Weissbourd, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, *The Transuranium Elements: Research Papers*, Paper No. 16.8 (McGraw-Hill Book Company, Inc., New York, 1949).

equipped with a fast sample-changing mechanism. Through the use of the latter, alpha-particle energies associated with the new collateral alpha-decay chains have been measured.

The collateral chains have been characterized by physical or chemical separation and identification of radioactive end-products of decay which are common both to the chain and to one of the four alpha-radioactive families. When the half-life was too short to allow chemical operations to be performed on a sample, it was possible to separate daughters from their alpha-parents by recoil methods[10] (see Appendix). Many chemical separations have also been made to establish the mass assignments of the series. Such separations[8] have been made for thorium, protactinium, actinium, bismuth, and lead to separate orbital electron capture, beta-, or alpha-decay daughters from the members of the series. In some cases where it has not been possible to perform these separations, assignment has been based on regularities in alpha-decay systematics.[11–13] In many cases where their half-lives and abundances have permitted, individual members of the chains have been studied.

In the next section each series will be discussed individually. The interrelation of each of the series can probably best be seen by reference to a nuclide chart of the heavy region such as is given in Fig. 1. The half-life values given are the most recent available.

III. RESULTS

As stated above, the data for these collateral chains have been previously presented in a preliminary form.[5–7] The experimental results, however, have been reworked completely since the previous reports were made and some additional experimental work has been included. Presented in Table I are the latest half-life and particle energy values (not total disintegration energies) for the five collateral series. Half-life and energy values in parenthesis have been estimated from alpha-decay systematics curves.[11–13] The values presented in this table supersede the values published previously. The radioactive properties of RaE, Po^{210}, AcC, AcC″, ThC, ThC″, ThC′, Po^{213}, and Pb^{209} are the accepted values taken from the literature.[7]

For easy reference, the values for each chain have been combined in Table I. The following discussion treats each chain separately.

A. The Pa^{226} Series

The protactinium fraction from a 150-Mev deuteron bombardment of thorium nitrate in the jiffy probe of the 184-inch cyclotron shows a series of four alpha-particle emitters immediately after bombardment. These activities decay with the 1.8-min half-life of the protactinium parent and appear to be members of a collateral branch of the uranium ($4n+2$) family as shown by dotted lines in the block diagram of Fig. 2.

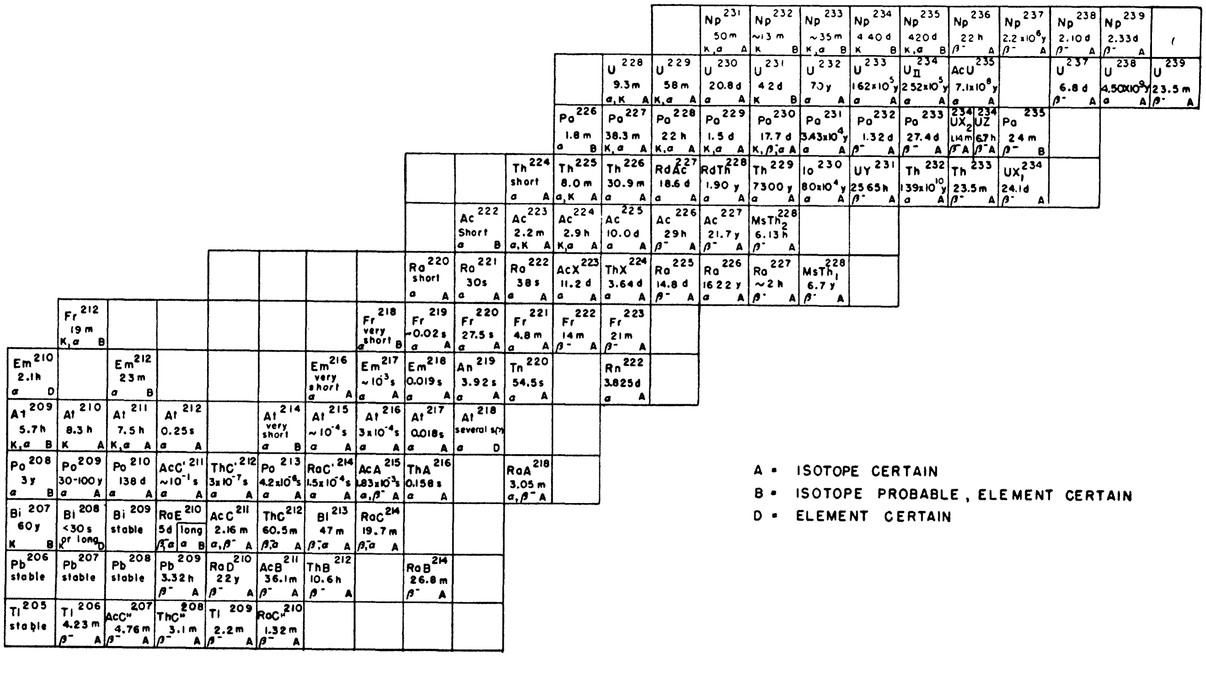

FIG. 1. Nuclide chart for a portion of the heavy region.

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[10] Rutherford, Chadwick, and Ellis, *Radiations from Radioactive Substances* (Cambridge University Press, London, 1930), third edition, p. 557.

[11] Perlman, Ghiorso, and Seaborg, Phys. Rev. **74**, 1730 (1948).

[12] Perlman, Ghiorso, and Seaborg, Phys. Rev. **75**, 1096 (1949).

[13] Perlman, Ghiorso, and Seaborg, Phys. Rev. **77**, 26 (1950), and unpublished revisions bringing curves up to date.

TABLE I. Collateral series data.

Nuclide	Type of radiation	Half-life	Energy of radiation (Mev)
		Pa^{226} series	
Pa^{226}	α	1.8 ± 0.2 min	6.81 ± 0.05
Ac^{222}	α	(pred. 30 sec)	6.96 ± 0.05
Fr^{218}	α	(pred. 5×10^{-3} sec)	7.85 ± 0.05
At^{214}	α	(pred. 2×10^{-6} sec)	8.78 ± 0.05
Bi^{210} (RaE)	β^-	5.0 days	1.17
Po^{210}	α	138 days	5.298
Pb^{206}	Stable		
		Pa^{227} series	
Pa^{227}	α (~85%) K (~15%)	38.3 ± 0.3 min	6.46 ± 0.02
Ac^{223}	α (99%) K (1%)	2.2 ± 0.1 min	6.64 ± 0.02
Fr^{219}	α	0.02 ± 0.002 sec	7.30 ± 0.02
At^{215}	α	10^{-4} sec, ±20%	8.00 ± 0.02
Bi^{211} (AcC)	α (99.7%)	2.16 min	6.619
Tl^{207} (AcC″)	β^-	4.76 min	1.47
Pb^{207}	Stable		
		Pa^{228} series	
Pa^{228}	α (~2%) K (~98%)	22 ± 1 hr	6.09 ± 0.02 (75%) 5.85 ± 0.02 (25%)
Ac^{224}	α (~10%) K (~90%)	2.9 ± 0.2 hr	6.17 ± 0.03
Fr^{220}	α	27.5 ± 1.5 sec	6.69 ± 0.03
At^{216}	α	3×10^{-4} sec ±10%	7.79 ± 0.03
Bi^{212} (ThC)	α (34%) β^- (66%)	60.5 min	6.081 (27%) 6.042 (70%) 2.20
Tl^{208} (ThC″)	β^-	3.1 min	1.72
Po^{212} (ThC′)	α	3×10^{-7} sec	8.776
Pb^{208}	Stable		
		U^{228} series	
U^{228}	α (~80% K (~20%)	9.3 ± 0.5 min	6.67 ± 0.01*
Th^{224}	α	(pred. 1 sec)	7.13 ± 0.02*
Ra^{220}	α	(pred. 3×10^{-2} sec)	7.43 ± 0.02*
Em^{216}	α	(pred. 10^{-4} sec)	8.01 ± 0.03*
Po^{212} (ThC′)	α	3×10^{-7} sec	8.776
Pb^{208}	Stable		
		U^{229} series	
U^{229}	α (~20%) K (~80%)	58 ± 3 min	6.42 ± 0.02
Th^{225}	α (~90%) K (~10%)	8.0 ± 0.5 min	6.57 ± 0.03
Ra^{221}	α	30 ± 2 sec	6.71 ± 0.03
Em^{217}	α	10^{-3} sec ±10%	7.74 ± 0.03
Po^{213}	α	4.2×10^{-6} sec	8.336
Pb^{209}	β^-	3.32 hr	0.70
Bi^{209}	Stable		

* Orth, Ghiorso, and Seaborg, unpublished work (1950).

Alpha-particle pulse analysis of a protactinium sample 3.3 min after the end of a 1.5-min bombardment indicated two series of alpha-particles (Fig. 3). One series decayed out rapidly, until, at the end of ten minutes, only the second series was present. The decay is shown in Fig. 4 by pulse analysis curves taken during the 10-min period. If the contribution of the 38.3-minute Pa^{227} series (to be discussed in the next section) is subtracted from Fig. 3, the alpha-peaks of the Pa^{226} series remain as in Fig. 5.

The mass type for the parent of the series has not yet been identified through known daughters in the main branch of the radioactive family. The requirements for yield, speed, and purity of samples from the chemical procedure are so stringent that with the present cyclotron beams and bombardment techniques, the task of separating enough 5-day Bi^{210} (RaE) from the decay of this series or of separating Th^{226} from the electron capture branching decay of the parent is almost prohibitively difficult. Furthermore, it has not been possible to date to assign absolutely any alpha-peak to a particular isotope of the series. When the method of formation and half-life of the protactinium parent and the energies of the four members of the series are considered in the light of known alpha-decay systematics, however, it becomes fairly certain that the assignment of isotopes to energies shown in Fig. 5 are valid. On this basis the series decays as follows:

$$Pa^{226} \xrightarrow[1.8\text{ min}]{\alpha} Ac^{222} \xrightarrow[\text{(predicted 30 sec)}]{\alpha}$$

$$Fr^{218} \xrightarrow[\text{(pred. } 5\times10^{-3}\text{ sec)}]{\alpha} At^{214} \xrightarrow[\text{(pred. } 2\times10^{-6}\text{ sec)}]{\alpha}$$

$$Bi^{210}\text{ (RaE)} \xrightarrow[5\text{ days}]{\beta^-} Po^{210} \xrightarrow[138\text{ days}]{\alpha} Pb^{206}\text{ (stable).}$$

1. Pa^{226}

Early attempts to find this isotope failed because the chemical procedures used to separate protactinium were too time consuming. With the development of faster techniques, the existence of a short-lived protactinium series was finally established by means of a full energy deuteron bombardment of 1-mil thorium metal foil mounted in the jiffy probe of the 184-inch cyclotron. The best separation time attained was six minutes, however; and always at the first count the Pa^{227} series activity was so overwhelming that half-life and energy measurements were extremely uncertain.

Finally, it was possible to reduce the separation time to 3.3 min by bombarding thorium nitrate in the jiffy probe. Related experiments[14] had shown that for (*d*, *xn*) reactions, the excitation function exhibits a sharp

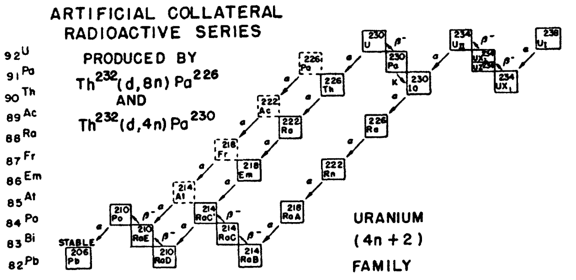

FIG. 2. Block diagram of the Pa^{226} collateral series.

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[14] Meinke, Wick, and Seaborg, University of California Radiation Laboratory Report UCRL-868 (September, 1950).

peak which makes the optimum yield of the product isotope very dependent upon the bombarding energy. This allows differentiation between neighboring isotopes in (d, xn) reactions. Bombardments with 150-Mev deuterons resulted in sufficient activity to give satisfactory pulse analyses, one of which is shown in Fig. 3. By following the decay of the longest range alpha-peak (assumed to be At^{214} from systematics), a half-life of 1.8 ± 0.2 min for the Pa^{226} was obtained.

In the further alpha-pulse analysis of the activity remaining after the decay of the Pa^{226} series, it was not possible to detect in the presence of the remaining Pa^{227} series any alpha-peaks due to 30-min Th^{226} and daughters arising from electron capture branching decay of Pa^{226}. Consequently, it is possible to set an upper limit of about one for the K/α branching ratio of Pa^{226}.

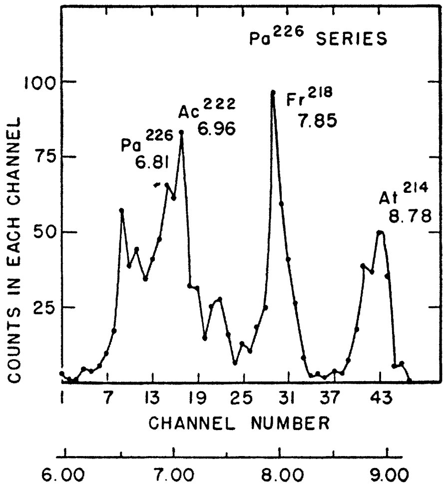

FIG. 3. Alpha-pulse analysis curve of the Pa^{226} series with some Pa^{227} series contamination. The collimated sample was counted for 0.5 min.

2. *Other Members of the Pa^{226} Series*

To date it has not been possible to obtain any data other than the half-life of the Pa^{226} and the alpha-energies of the members of the series. The assignments of mass numbers to these daughter isotopes is made on the basis of alpha-energy *vs* mass number systematics.

B. The Pa^{227} Series

Shortly after 80-Mev deuteron bombardment of thorium, a number of alpha-groups are prominent in the pulse analysis of a protactinium chemical fraction. These groups decay with the 38.3-min half-life of the parent and dominate pulse analyses of protactinium fractions for from five to six hours after the end of bombardment before other alpha-groups make their appearance.

The groups have been definitely assigned to the Pa^{227} series, a collateral branch of the actinium $(4n+3)$ family as shown in the block diagram of Fig. 6. The alpha-pulse analysis of the five alpha-groups in this series is presented in Fig. 7.

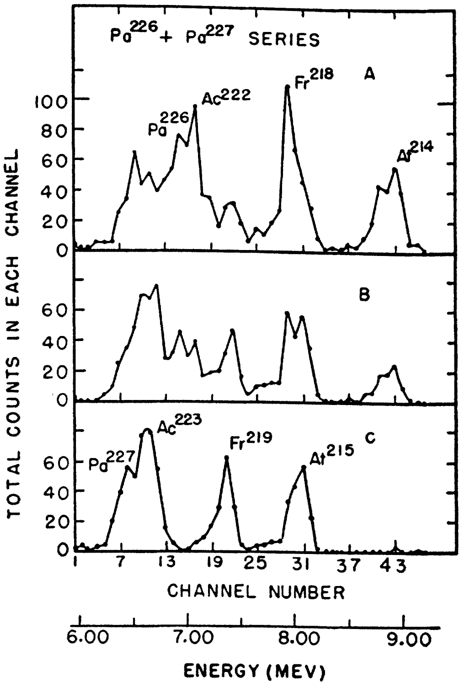

FIG. 4. Alpha-pulse analysis curves showing the decay of the Pa^{226} series, leaving the Pa^{227} series. The curves represent 0.5-min counts of the collimated sample started at the following times after the end of bombardment: A, 3.3 min; B, 6.0 min; C, 10.5 min.

The mass assignment of the series was established by chemically separating electron capture decay products of the first and second members of the series, as well as by the identification of the Bi^{211} (AcC) and Tl^{207} (AcC″) daughters. A half-life value has been obtained for each member of the series and in addition, assignment of the

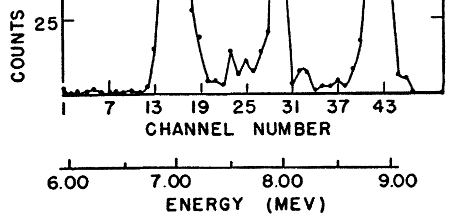

FIG. 5. Resolved alpha-pulse analysis curve of the Pa^{226} series from which the Pa^{227} series peaks shown in Fig. 3 have been subtracted.

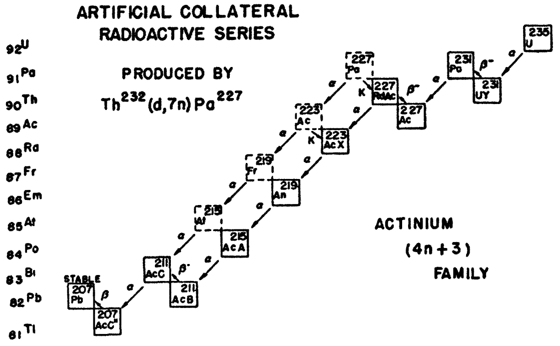

FIG. 6. Block diagram of the Pa^{227} collateral series.

alpha-energies to the nuclides has been made experimentally. Since it is not found in pulse analysis of single recoil samples from the Pa^{227} series, the 6.46-Mev alpha-peak is assigned to Pa^{227}. Also, it has been possible by the method of delayed coincidences to prove electronically that the 7.30-Mev alpha-particle follows the 6.64-Mev particle, and that the 8.00-Mev alpha-particle follows the 7.30-Mev particle.

This work, then, has definitely established that the series is the Pa^{227} series which decays in the following manner:

$$\mathrm{Pa}^{227} \xrightarrow[38.3\text{ min}]{\alpha} \mathrm{Ac}^{223} \xrightarrow[2.2\text{ min}]{\alpha} \mathrm{Fr}^{219} \xrightarrow[0.02\text{ sec}]{\alpha} \mathrm{At}^{215} \xrightarrow[10^{-4}\text{ sec}]{\alpha}$$

$$\mathrm{Bi}^{211}\ (\mathrm{AcC}) \xrightarrow[2.16\text{ min}]{\alpha}$$

$$\mathrm{Tl}^{207}\ (\mathrm{AcC''}) \xrightarrow[4.76\text{ min}]{\beta^-} \mathrm{Pb}^{207}\ (\text{stable}).$$

The branches which arise from orbital electron capture by Pa^{227} and Ac^{223} are not shown.

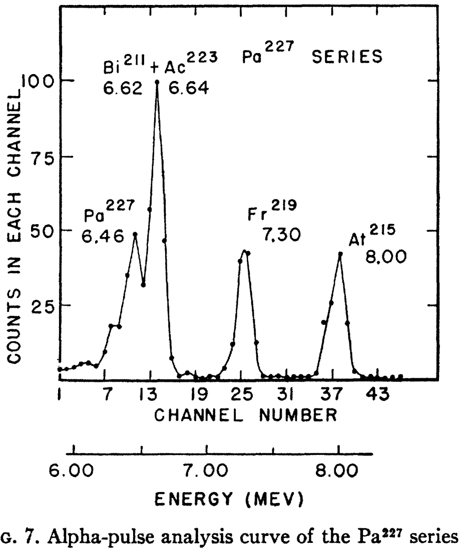

FIG. 7. Alpha-pulse analysis curve of the Pa^{227} series.

1. Pa^{227}

Since it is possible to obtain this isotope in very high yield and since it is the only protactinium isotope in evidence for a period of five or six hours after bombardment, it has been possible to do many experiments with this isotope. The half-life was determined to be 38.3 ± 0.3 min by following the decay of the gross alpha-counts of the series of alpha-emitters. As the main protactinium fraction decayed, aliquot fractions were taken and chemically purified from the daughter radioactivities of 22-hr Pa^{228} also present in the sample (see below); a number of decay points of the Pa^{227} (plus equilibrium daughter products) alpha-activity were taken on each purified aliquot before sufficient daughter activity from the Pa^{228} present made it necessary to purify another aliquot.

By chemically separating a sample of thorium (including Th^{230} as tracer to determine chemical yield) from the decay products of a known amount of Pa^{227}, the K/α branching ratio of this isotope was determined. The Pa^{227} which had been purified from thorium was allowed to decay in a solution of thenoyltrifluoroacetone[15] (TTA) in benzene for 40 min. The daughters were washed from the organic layer with nitric acid and this acidic aqueous solution was washed three times with fresh TTA-benzene solution to extract any protactinium contamination which had been removed from the original organic layer. Correction was made for the time this contaminating protactinium decayed while in the acid solution. The Pa^{227} was allowed to decay only one half-life in the organic solution to reduce the amount of Th^{228} present from the large orbital electron branching decay of 22-hr Pa^{228} (present also in the sample). For a 60-Mev deuteron bombardment when this amount of decay was allowed, pulse analysis showed twice as much Th^{227} as Th^{228} present in the separated daughters. The yield of the 18.6-day Th^{227} in the separated sample indicated a K/α ratio of 0.18 ± 0.02 for Pa^{227}.

Further evidence that the Th^{227} came from the 38.3-min protactinium isotope was obtained when successive separation of thorium from the protactinium sample indicated that the parent of the Th^{227} was decaying with a half-life of about 35 min. The slight discrepancy in half-lives is due to a small loss of parent in the chemical separations.

A double (or second-order) recoil experiment was performed to produce a sample of the well-known nuclide, Bi^{211}, which could be pulse-analyzed free from its parent activities. This was done by first collecting Ac^{223} and daughter atoms by alpha-recoil from Pa^{227} and then Bi^{211} atoms by alpha-recoil from this first recoil sample (the francium and astatine intermediates, of course, do not interfere because of their short half-lives). It was thus possible to observe the Bi^{211} 6.62-Mev alpha-

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[15] J. C. Reid and M. Calvin, U. S. Atomic Energy Commission Declassified Document MDDC-1405 (August 13, 1947); also, J. Am. Chem. Soc. 72, 2948 (1950).

particle energy and 2.16-min decay. Furthermore, it was possible by a triple (or third-order) recoil experiment utilizing a very large sample of Pa^{227} to collect enough of the Tl^{207} daughter to follow its 4.76-min decay, and even to make rough aluminum absorption measurements to check its energy. Hence, the assignment of this series to Pa^{227} is established beyond doubt.

Absolute cross sections or relative yields for this isotope have been determined for several methods of production: the $Th^{232}(p, 6n)Pa^{227}$, $Th^{232}(d, 7n)Pa^{227}$, $Th^{232}(\alpha, p8n)Pa^{227}$, and $U^{238}(p, \alpha 8n)Pa^{227}$ reactions.[14] The excitation functions for these reactions have been studied with full energy particles from the 184-inch cyclotron and are reported in detail in another paper.[14]

2. *Ac*^{223}

Recoil atoms collected from samples containing the Pa^{227} series decayed by alpha-emission with a half-life of about 2.5 min. This value, however, is a composite one due to Ac^{223} and the 2.16-min Bi^{211} daughter. Since the half-lives of these two isotopes are so similar, it was impossible by this method to resolve one from the other.

Another method of attack was more successful in determining the half-life of this isotope. From a plate containing the Pa^{227} series, recoil atoms were collected for ten minutes, long enough to ensure equilibrium between the activity on the sample plate and that on the collector plate. The collector was then removed and successive 1-min recoil samples collected from it over a period of about ten minutes. The decay of the Bi^{211}, the only alpha-activity present on the second-order recoil plates, was followed for about two minutes for each sample. All the counting of successive second-order recoil samples was done on the same alpha-counter and the counts were recorded automatically on tape. The best 2.16-min lines were used to extrapolate the decay rates of each of the second-order recoil plates containing Bi^{211} back to the times of separation from the Ac^{223} parent. These extrapolated values were plotted as ordinates against the time in minutes after removal of the first recoil collecting plate from its Pa^{227} parent. The half-life of Ac^{223} as determined by this method is 2.2 ± 0.1 min. The only assumption made was that the efficiency of recoil was constant during the ten minutes of the experiment. This assumption appears reasonable since the geometry and electric collection field remained the same.

Data on the branching ratio of this isotope were also obtained from recoil experiments. A very large sample of Pa^{227} and daughters (probably about 10^9 or more alpha-counts per minute) was used as the parent for a 10-min collection of recoil fragments. This sample of recoil fragments was allowed to decay for about 15 days and was finally subjected to alpha pulse analysis to determine the amount of Ra^{223} present. The alpha-pulse analysis was somewhat complicated, since the sample also contained Ra^{224} and Ac^{225} as alpha-recoil daughters of Pa^{228} (via Th^{228} and Ac^{224}) and Pa^{229}, respectively.

The activities due to Ra^{224} and Ac^{225} (whose alpha-energies are similar to that of Ra^{223}) were determined from the intensity of their long range daughters, Po^{212} and Po^{213}; the Ra^{223} activity which had been formed from the orbital electron capture of Ac^{223} was then determined by subtraction.

The number of recoiling Ac^{223} atoms collected from the Pa^{227} sample was estimated in the following manner. Recoil samples were collected for a period of several seconds from the parent Pa^{227} sample and then followed for decay in an alpha-counter. The plotted Ac^{223} and Bi^{211} equilibrium decay lines were then extrapolated back to the end of the recoil growth times and these values plotted. Three such samples were taken and the best 38.3-min line drawn through them; a point on this line at the middle of the growth period of the large recoil sample gave an indication of the amount of activity that was recoiling to the collection plate at that time. It was then assumed that 1/7 of this gross alpha-recoil activity was due to Ac^{223} alpha-particles. The reason for this assumption is as follows. Whenever an Ac^{223} atom is recoiled over, there are four alpha-emitting isotopes which may be counted; whenever a Fr^{219} atom recoils over, there is only the one Bi^{211} alpha which may subsequently be counted, since Fr^{219} and At^{215} are very short-lived; and similarly, whenever an At^{215} or a Bi^{211} atom is collected, there is only the possibility of counting the alpha-emission from Bi^{211}. If we assume that the efficiency of recoil is independent of the alpha-energy of the parent atom, then it can be seen that the equilibrium mixture of alpha-activities in the recoil sample will consist of one part due to Ac, one due to Fr, one to At, and four to Bi.

This comparison of the number of atoms decaying by alpha-emission and the number by orbital electron capture shows that the K/α branching ratio for Ac^{223} is ~ 0.01. (Note: This value differs by a factor of 10 from the value presented in the Table of Isotopes.)[7]

3. *Fr*^{219}

From alpha-decay systematics, a short half-life is expected for this isotope. A determination using the delayed coincidence method described in the Appendix gave a value of about 20 msec which is accurate to within about 10 percent.

In order to check both this value and the feasibility of a rotating disk recoil method for the measurement of short half-lives (also described in the Appendix), a sample containing about 4×10^6 alpha-counts per minute of Pa^{227} was mounted above a disk which was rotating at a speed of one revolution per second. The recoiling Fr^{219} atoms were collected on the disk and some of these consequently emitted alpha-particles into an alpha-counting chamber displaced successively at three different distances from the Pa^{227} sample. The half-life of this francium isotope as determined by this method was approximately 20 msec.

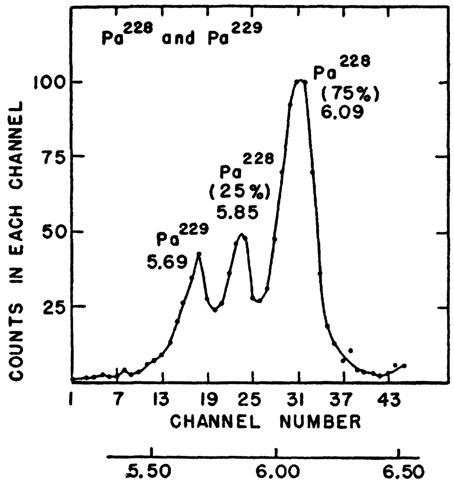

FIG. 8. Alpha-pulse analysis curve of the Pa^{228} and Pa^{229} alpha-groups after complete decay of the Pa^{227} series. This sample was purified from daughter activities immediately before counting.

4. At^{215}

The half-life of this isotope has been determined electronically by the method of delayed coincidences to be about 10^{-4} sec, within about 20 percent.

It is interesting to note that the energy obtained for the At^{215} alpha-particles is several hundred kilovolts less than the 8.4-Mev value reported by Karlik and Bernert[16] for At^{215} as formed by the beta-particle branching decay of Po^{215} (AcA).

C. The Pa^{228} Series

After the Pa^{227} series has decayed, freshly purified protactinium samples exhibit three prominent alpha-peaks in pulse analysis curves, as shown in Fig. 8. Two of these are due to Pa^{228} and the other to Pa^{229}. The isotope Pa^{229} is known[7,17] to be a 1.5-day alpha-emitter and grows the 10.0-day Ac^{225} and subsequent short-lived daughters. Pa^{228} is a new isotope and grows, by alpha-decay, a previously unknown alpha-emitting chain collateral to the thorium ($4n$) family as shown in the block diagram of Fig. 9 (which also includes the U^{228} collateral series which is to be discussed later). In practice, it is difficult to observe the 2.9-hr Ac^{224} and other daughters from the alpha-emission of Pa^{228}. In the present cyclotron bombardments the yields of 17-day Pa^{230} from the (d, $4n$) reaction on thorium were always very much higher than those for the (d, $6n$) reaction; consequently, because of the beta-decay of Pa^{230}, the members of the Pa^{230} series[18] would quickly become prominent and interfere with measurements on the members of the Pa^{228} series.

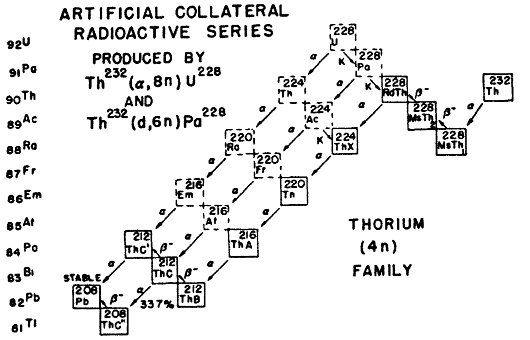

FIG. 9. Block diagram of the Pa^{228} and U^{228} collateral series.

The alpha-decay daughters of Pa^{228} were separated by recoil experiments. Shown in Fig. 10 is a pulse analysis curve measured on a first recoil sample which has been taken from a sample containing Pa^{228}, Pa^{229}, and Pa^{230} after the daughters of the Pa^{228} had come into equilibrium with the parent. Here we see the uncontaminated alpha-peaks of Ac^{224} and daughters, since Th^{226} had been allowed to decay completely. Further recoil experiments showed that a 27.5-sec activity followed that due to Ac^{224}, and delayed coincidence experiments showed that the Fr^{220} isotope with the 6.69-Mev alpha-particle is the parent of the At^{216} isotope with the 7.79-Mev alpha-particle. Hence, the Pa^{228} series decays in the following manner:

$$Pa^{228} \xrightarrow[\text{22 hr}]{\alpha} Ac^{224} \xrightarrow[\text{2.9 hr}]{\alpha} Fr^{220} \xrightarrow[\text{27.5 sec}]{\alpha} At^{216} \xrightarrow[3\times10^{-4}\text{ sec}]{\alpha}$$

$$Bi^{212}\,(ThC) \begin{array}{c} \xrightarrow[\text{34 percent}]{\alpha} Tl^{208}\,(ThC'') \xrightarrow[\text{3.1 min}]{\beta^-} \\ \text{60.5 min} \\ \xrightarrow[\text{66 percent}]{\beta^-} Po^{212}\,(ThC') \xrightarrow[3\times10^{-7}\text{ sec}]{\alpha} \end{array} Pb^{208}\text{ (stable).}$$

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[16] B. Karlik and T. Bernert, Naturwiss. 32, 44 (1944).

[17] Hyde, Studier, Hopkins, and Ghiorso, National Nuclear Energy Series, Plutonium Project Record, Vol. 14*B*, *The Transuranium Elements: Research Papers*, Paper No. 19.17 (McGraw-Hill Book Company, Inc., New York, 1949).

[18] M. H. Studier and E. K. Hyde, Phys. Rev. 74, 591 (1948).

The branches which arise from orbital electron capture by Pa^{228} and Ac^{224} are not shown.

Measurements on a chemically separated lead-bismuth fraction from an equilibrium mixture of the Pa^{228} series confirmed the presence of the Pb^{212} (ThB), Bi^{212} (ThC), and Po^{212} (ThC′) members of the thorium family and hence confirmed the mass assignment of the series.

1. *Pa*^{228}

In the measurement of the half-life of Pa^{228} there arises the problem of resolution of pulse analysis curves, since the 1.5-day Pa^{229} is always found with Pa^{228} to some extent. Even when a bombardment is planned for maximum Pa^{228} and minimum Pa^{229} yield, there will not be a difference of more than about 20 between the yields of the two isotopes; and by the time the Pa^{228} has decayed for one or two half-lives, the Pa^{229} activity will become appreciable and affect the decay curve; Fig. 8 shows a pulse analysis curve from the protactinium fraction of a typical bombardment.

Since the energies of the Pa^{228} and Pa^{229} are quite close together [6.09 Mev (75 percent) and 5.85 Mev (25 percent) for the two groups of Pa^{228} and 5.69 Mev for Pa^{229}], resolution of consecutive pulse analyses is difficult and inaccurate. A preliminary value of 22 hours was obtained from a rough resolution of several successive pulse analyses taken over a period of two half-lives of the Pa^{228}. In this method, however, there is no good opportunity to estimate the error or to observe trends in the half-life measurements, and it was consequently discarded.

Another method consisted of counting all the alpha-particles in the entire group of peaks representing the Pa^{228} and Pa^{229} from pulse analysis measurements and obtaining the ratio of these counts to long-lived Pa^{231} tracer added at the beginning of the experiment. These counts were taken at about 12-hr intervals and the ratios plotted to represent the composite decay. New samples which had been freshly separated from their daughters were used for each point and thus the use of tracer Pa^{231} was imperative. This chemical separation was necessary in order to remove the Pa^{230} series alpha-particle peaks which tend to obscure the Pa^{228} and Pa^{229} peaks. Figure 12 represents the decay of the sum of the alpha-particles in the Pa^{229} and Pa^{228} peaks, while Fig. 11 shows representative pulse analyses taken at the beginning, in the middle, and near the end of the decay experiment. The dotted line resolution indicated in Fig. 12 represents the intensity of Pa^{229} alpha-particles obtained from the data shown in Fig. 11C (9-day sample) together with a 1.5-day slope corresponding to the half-life of Pa^{229}. This Pa^{229} line was then subtracted from the original points and a line with a slope corresponding to a half-life of 21.8 hr for Pa^{228} was obtained. Other methods of treating the data gave slightly different values for the half-life of Pa^{228}, but all of these values are consistent with a half-life of 22±1 hr for this isotope.

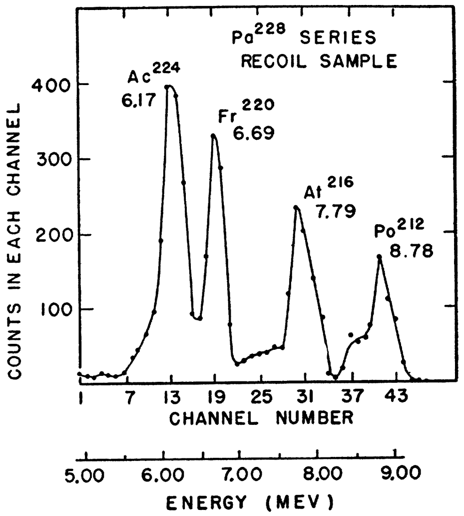

FIG. 10. Alpha-pulse analysis curve of Ac^{224} and alpha-daughters obtained with a recoil sample from Pa^{228}.

Chemical separation of 1.9-yr Th^{228} after the decay of a known amount of Pa^{228} was made to determine its branching ratio for electron capture. An aliquot of the original Pa^{228} solution was subjected to pulse analysis in order to determine the amount of Pa^{228} present. Tracer

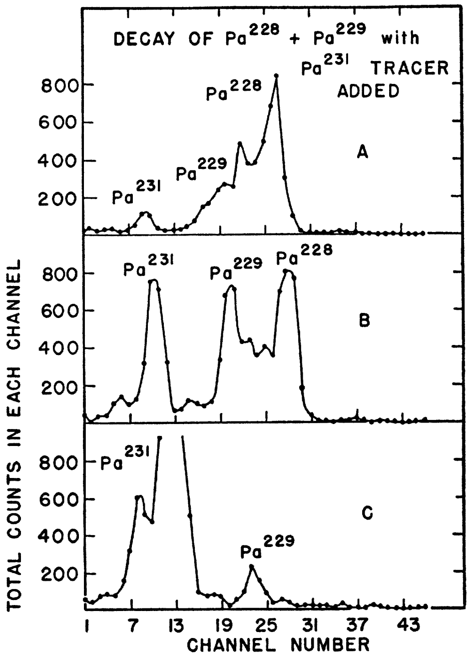

FIG. 11. Alpha-pulse analysis curves showing the decay of the Pa^{228} and Pa^{229} alpha-peaks relative to the long-lived Pa^{231} tracer peak. The curves represent different length counts of the freshly separated sample started at the following times after the end of bombardment: A, 10 hours; B, 3.05 days; C, 9.05 days. (The energy scale has been shifted for curve C.)

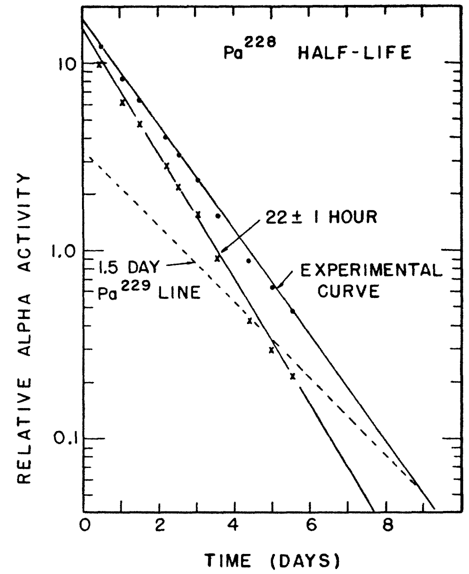

FIG. 12. Determination of the Pa^{228} half-life by measurement of decay of resolved and summed Pa^{228} and Pa^{229} pulse-analysis peaks.

Th^{230} was added and the sample was allowed to decay for six days before thorium was chemically separated. The plates containing the thorium were pulse analyzed to determine the ratio of Th^{228} to Th^{230}. The value obtained for the K/α ratio for this isotope is 53±5.

2. Ac^{224}

The alpha-energy and half-life of this isotope were determined with a sample which was made by separating chemically an actinium-thorium fraction from an equilibrium mixture of Pa^{228} and its daughters.

The half-life value obtained by following the decay of this activity agrees with the value of 2.9±0.2 hr found by determining the rate of decay of the At^{216} peak using pulse analysis curves obtained from measurements on a recoil sample from Pa^{228}; an example of such curves is shown in Fig. 10.

By pulse analysis measurements on recoil samples from a large amount of Pa^{228}, it was possible to determine the alpha-disintegration rate of the Ac^{224} present and later to determine the amount of the orbital electron capture daughter Ra^{224} present after complete decay of the Ac^{224}. Although resolution of the pulse analysis curves was rather difficult, a value for the K/α branching ratio of Ac^{224} of 10±2 was obtained (two determinations gave 8.8 and 11.6). It was determined that only a negligible amount of Ra^{224} was present in the sample owing to the recoil from the 1.9-year Th^{228} which had grown into the original parent sample.

3. Fr^{220}

Experiments on recoil fractions led to a half-life of 27.5±1.5 sec for this isotope. From a large sample of Pa^{228}, recoil samples were collected for short periods of time and followed for gross alpha-decay in a conventional alpha-counter. The resolved decay curve is shown in Fig. 13. In these experiments the contribution of the Ra^{222} which was present in low abundance from the Pa^{230} series was negligible.

4. At^{216}

The half-life for this isotope, as measured by the delayed coincidence method, was found to be about 300 μsec. It is interesting to note the correspondence between the energy of these At^{216} alpha-particles (7.79 Mev) and the energy (7.64 Mev) reported by Karlik and Bernert[19] for At^{216} as formed by the beta-particle branching decay of Po^{216} (ThA). However, there seems to be good reason to doubt the beta-instability of ThA (see Perlman, Ghiorso, and Seaborg[13] for a discussion of this point).

D. The U^{228} Series

Shortly after bombardment of thorium with 120-Mev helium ions, the uranium fraction contains a series of five alpha-emitters which decay with the 9.3-min half-life of the uranium parent, which is apparently a collateral branch of the thorium (4*n*) family as shown in Fig. 9. As this series decays, the 58-min U^{229} series (discussed below) is left from the original mixture as shown in Figs. 14 and 15.

The assignment of masses to this series is difficult, since the only known member of a natural radioactive family present with it is the very short-lived Po^{212} (ThC′).

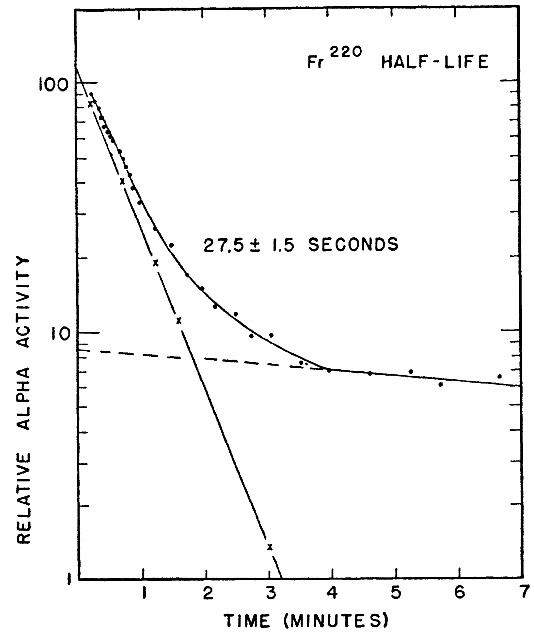

FIG. 13. Determination of the half-life of Fr^{220} from gross decay of recoil samples from a sample containing a large amount of the Pa^{228} series.

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[19] B. Karlik and T. Bernert, Naturwiss. 31, 492 (1943).

However, in addition to the energy identification of the high energy Po^{212} alpha-particles, further proof of the mass assignment has been obtained by chemically separating Pa^{228} as the orbital electron capture daughter of the U^{228}. Hence, it is established that this series begins with the U^{228} isotope; and, with the help of alpha-decay systematics, the following decay sequence is suggested:

$$\mathrm{U}^{228} \xrightarrow[9.3\ \text{min}]{\alpha} \mathrm{Th}^{224} \xrightarrow[\text{(pred. 1 sec)}]{\alpha}$$

$$\mathrm{Ra}^{220} \xrightarrow[\text{(pred. } 3\times10^{-2}\text{ sec)}]{\alpha} \mathrm{Em}^{216} \xrightarrow[\text{(pred. } 10^{-4}\text{ sec)}]{\alpha}$$

$$\mathrm{Po}^{212}\ (\mathrm{ThC}') \xrightarrow[3\times10^{-7}\text{ sec}]{\alpha} \mathrm{Pb}^{208}\ \text{(stable)}.$$

The branch arising from the electron capture decay of U^{228} is not shown.

1. U^{228}

The half-life of this isotope was determined as 9.3±0.5 min by following the decay of the alpha-activity in the Th^{224} and Ra^{220} peaks resolved from pulse analysis curves. The decay of the alpha-activity in the Po^{212} peak gave a half-life which was slightly shorter, but within the error of the measurements.

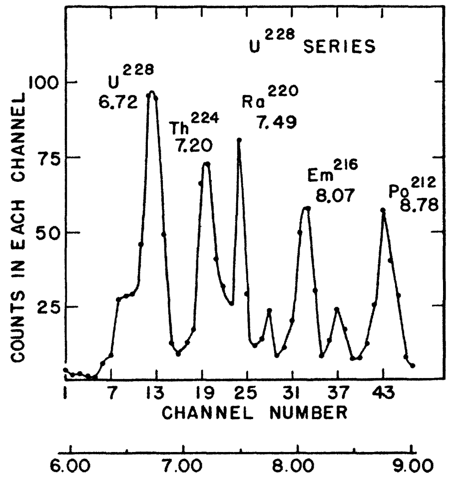

FIG. 14. Alpha-pulse analysis curve of the U^{228} series. Contaminating peaks are those of the U^{229} series. More accurate energy values from another source are given in the text.

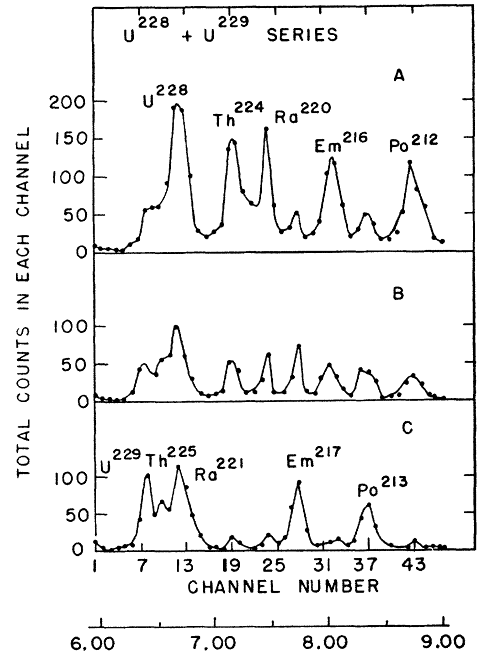

FIG. 15. Alpha-pulse analysis curves showing the decay of the U^{228} series in the presence of the longer-lived U^{229} series. Curves A and B represent 2-min counts, curve C, a 4-min count. Counts of the collimated sample were started at the following times after the end of bombardment: A, 21 min; B, 36 min; C, 65 min.

In order to determine the amount of electron capture branching decay of U^{228}, it was necessary to separate chemically Pa^{228} from the decay products of a large sample, after first having taken special precautions to remove by means of TTA-benzene extractions all Pa^{228} formed in the original bombardment. The chemical procedure involved separation of the uranium fraction from a 10-min bombardment of thorium metal through the use of ether extraction from saturated ammonium nitrate solution; the ether was washed with three portions of saturated ammonium nitrate, and finally the uranium was extracted back into pure water. The water solution was then made 6N in nitric acid and was contacted three times with double volumes of TTA-benzene solutions to eliminate any small traces of Pa^{228} which might have come through with the uranium in the ether extraction procedure. Some Pa^{231} was then added as tracer for chemical yield for the subsequent operation, and a small aliquot of the water solution was taken for pulse analysis and determination of the intensity of the U^{228} activity. After standing 20 min, the solution was again contacted with a TTA-benzene solution, this time to extract the daughter Pa^{228}, and the organic layer was evaporated on platinum, flamed, and counted.

It is difficult to obtain a sufficient amount of activity and to make the separations rapidly enough to perform this extraction operation successfully. The results of the experiment are rather indefinite, since the final plate containing the protactinium gave only about 0.4 counts/min of Pa^{228} with 73 percent recovery of the tracer. Consequently, the ratio of K/α reported in Table I as 0.25 may be in error and is presented principally as evidence that there is some orbital electron capture branching in this isotope.

2. *Other Members of the* U^{228} *Series*

The half-lives of the other members of this series have not yet been investigated. The assignment of alpha-energies to isotopes has been made from alpha-sys-

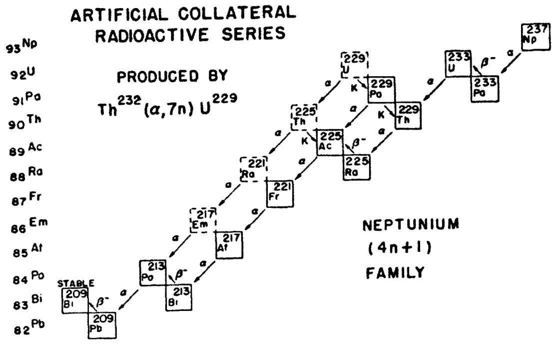

FIG. 16. Block diagram of the U^{229} collateral series.

tematics. Subsequent alpha-energy measurements by Orth, Ghiorso, and Seaborg (unpublished, 1950) on the alpha-decay chain of U^{228} as obtained from the 22-min Pu^{232} have given more accurate values than those shown in Fig. 14, and have been used in Table I of this paper.

E. The U^{229} Series

After the decay of the U^{228} series described above, there is readily apparent a second group of alpha-particle emitters which is collateral to the artificial, neptunium ($4n+1$), radioactive family[4] (Fig. 16). Alpha-pulse analysis shows a spectrum with three poorly resolved short-range peaks and two longer range ones as shown in Fig. 17. The best values for the energies were obtained from other curves not shown here. This 58-min series dominates the pulse analyses of uranium samples from these thorium bombardments for several hours before finally giving way to the U^{230} series as shown in Fig. 18. Chemical separation of 1.5-day Pa^{229} and 10.0-day Ac^{225} as orbital electron capture daughters of the U^{229} and the Th^{225} isotopes, respectively, proved the mass assignment and decay sequence of this series to be:

$$U^{229} \xrightarrow[58\text{ min}]{\alpha} Th^{225} \xrightarrow[8.0\text{ min}]{\alpha} Ra^{221} \xrightarrow[30\text{ sec}]{\alpha} Em^{217} \xrightarrow[10^{-3}\text{ sec}]{\alpha}$$

$$Po^{213} \xrightarrow[4.2\times 10^{-6}\text{ sec}]{\alpha} Pb^{209} \xrightarrow[3.32\text{ hr}]{\beta^-} Bi^{209}\text{ (stable)}.$$

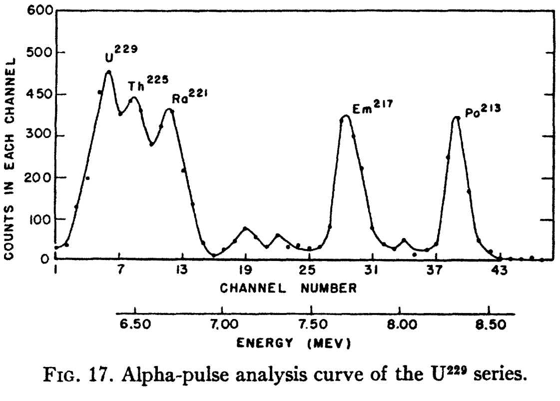

FIG. 17. Alpha-pulse analysis curve of the U^{229} series.

The branches arising from orbital electron capture of the U^{229} and Th^{225} are not shown.

1. U^{229}

The half-life of U^{229} was found to be 58 ± 3 min by following the decay of the alpha-counts in the U^{229}, Th^{225}, and Ra^{221} peaks. The resolved decay curve is shown in Fig. 19.

For the purpose of checking the electron capture branching ratio of this isotope, the daughter Pa^{229} was separated by a chemical procedure patterned after that used for the similar experiment with U^{228}. In order to eliminate any slight effect due to the Pa^{228} daughter of U^{228}, the target was allowed to stand for one hour after the end of the cyclotron bombardment. The uranium fraction was purified with three ammonium nitrate washes, and after extraction into water was subjected to further purification from protactinium by four washes with TTA-benzene solution. Tracer Pa^{231} was added and the sample then allowed to decay for 3.5 hr; at the end of this time the protactinium was separated by extraction into TTA-benzene, and the ratio of the alpha-activity of the Pa^{231} tracer to that of Pa^{229} was determined with the differential pulse analyzer. A value for K/α of about 5 (assuming the K/α ratio of Pa^{229} is 100) was obtained with an uncertainty largely dependent on the determination of the initial amount of U^{229} in the sample.

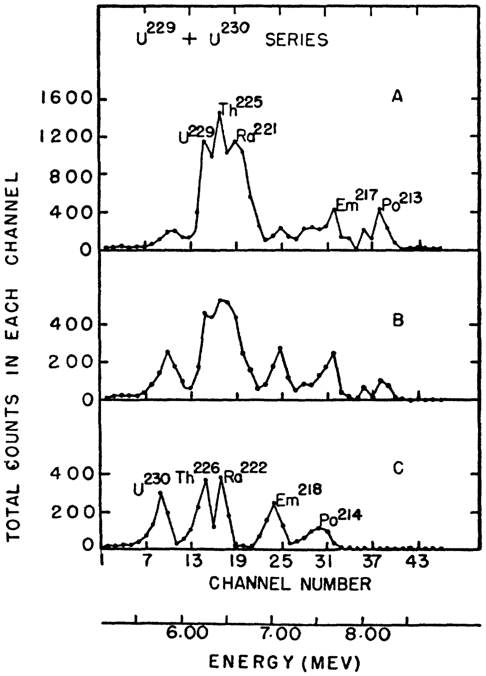

FIG. 18. Alpha-pulse analysis curves showing the decay of the U^{229} series in a mixture including the longer-lived U^{230} series. The curves represent counts of the noncollimated sample started at the following times after the end of bombardment: A, 1 hr; B, 4 hr; C, 8 hr. (The energy scale has been shifted for curve C.)

2. *Th*^{225}

The half-life of Th^{225} was determined by following the decay of the Po^{213} peak in pulse analyses of several recoil samples grown for a short time from a large amount of U^{229}; a value of 8.0±0.5 min was found.

The K/α branching ratio of this isotope was found by a method similar to that used for Ac^{223}. A recoil sample was grown for 3.5 hr from a plate containing the members of the U^{229} series. The short-lived activities were allowed to decay during a period of 9.5 days before an alpha-pulse analysis was made to determine the amount of 10.0-day Ac^{225} that had grown from Th^{225}. The amount of Th^{225} daughter activity which recoiled from the U^{229} plate was determined by several short recoil experiments performed in the same manner as those involving Ac^{223}.

The sample of U^{229} (*ca* 2×10^4 alpha-counts/min) was not as active as is desirable for this type of experiment, however, since only 0.4 alpha-counts/min of Ac^{225} were found on the collection plate originally containing Th^{225} and daughters. The value of 0.12 for the K/α branching ratio of this isotope is thus subject to a large possible error.

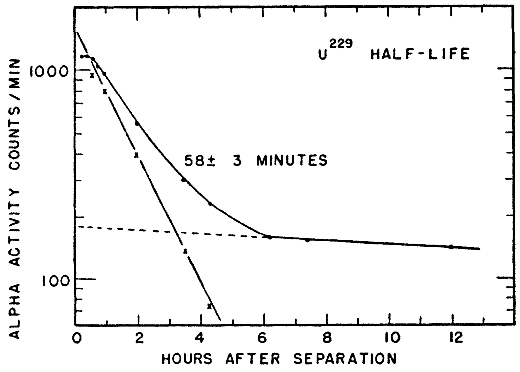

FIG. 19. Determination of the half-life of U^{229} from the decay of the alpha-activity in the U^{229}, Th^{225}, and Ra^{221} peaks from pulse analysis curves shown in part in Fig. 18.

3. *Ra*^{221}

Two types of recoil experiments were made to measure the 30±2-sec half-life of this isotope. A half-life value of 31.7 sec (Fig. 20) was obtained by the rotating disk method (described in Appendix). These points have been corrected for the decay of the parent during the time of the experiment and also for the 25 percent contamination of 38-sec Ra^{222} introduced from the U^{230} series which was present in the sample with the U^{229} series.

In the other method the recoil sample was transferred manually to an alpha-counter and its decay followed. Counts were taken every 0.05 min and recorded automatically on tape. With a relatively low counting rate and such a short interval between counts, the statistical fluctuations are quite large. In order to minimize these fluctuations, these data have been plotted on an integral curve in Fig. 21. Each count was corrected for background, and the values summed up to a time t. The summation of counts were plotted against t, and the value which they approached was taken as N_∞. In the integral curve, then, the difference between N_∞ (the total number of counts observed on complete decay) and N_t (the total number of counts observed to a certain time t) was plotted. The plot of this quantity on a logarithmic scale against time determines a half-life of 30±2 sec for the activity.

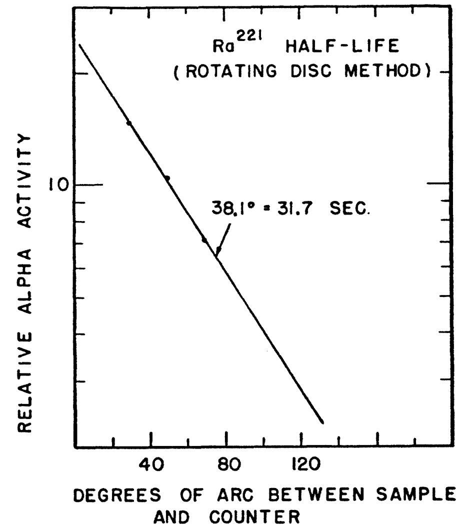

FIG. 20. Determination of the half-life of Ra^{221} by the rotating disk recoil method.

4. *Em*^{217}

The half-life of this isotope has been determined to be 1 msec, within about 10 percent, by the method of

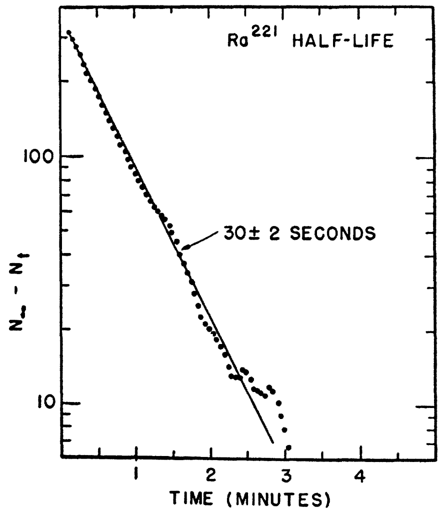

FIG. 21. Decay curve of Ra^{221}. N_∞ = total number of observed counts. N_t = number of observed counts within the time interval t.

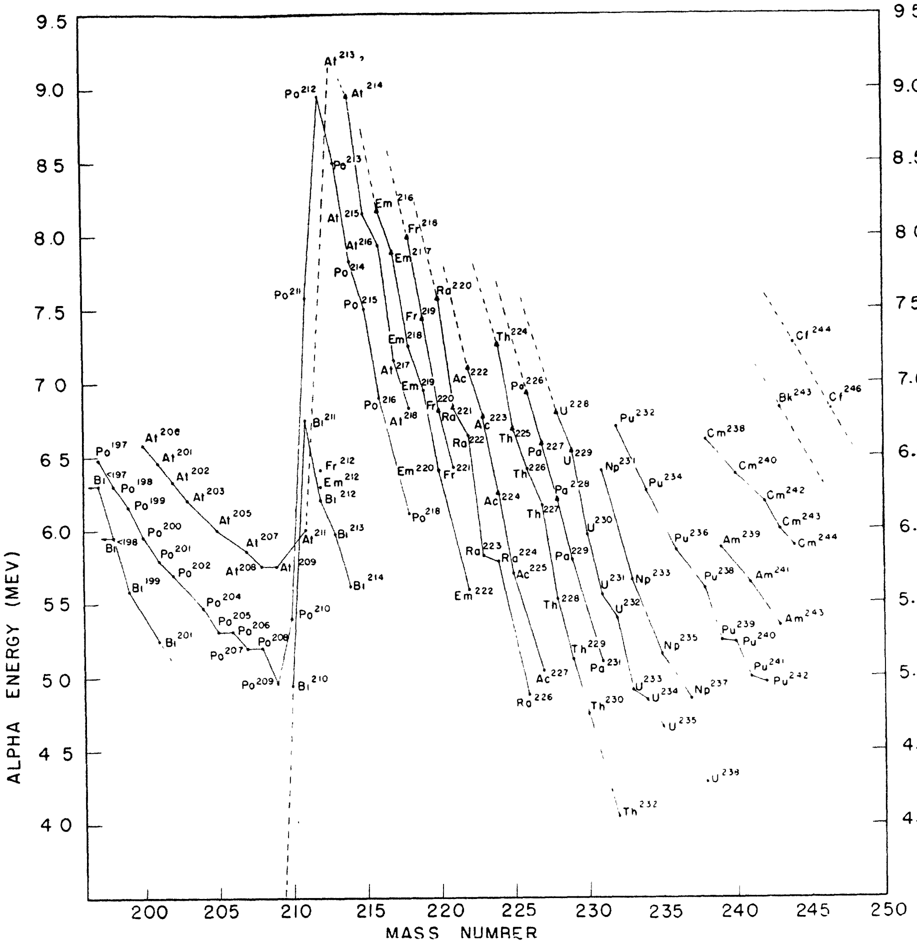

FIG. 22. Alpha-disintegration energy *vs* mass number relationships of the heavy nuclides. △ indicates points which represent data from the research described in the present paper.

counting delayed coincidences (described in Appendix) between the parent Ra^{221} and daughter Em^{217}.

IV. DISCUSSION

The present data have made a substantial contribution to the general study of systematics of alpha-decay properties and have already been extensively used and placed in the proper perspective in this connection.[13] Although the present discussion will not attempt to treat the subject in detail, a few points will be dealt with. It will be convenient for this purpose to use the plot of the alpha-disintegration energy *vs* mass number shown in Fig. 22. In this case the energy plotted corresponds to the total *alpha-disintegration energy*, that is, the total energy of transition between ground states, including the energy of the recoiling product nucleus. This is essentially a reproduction of Fig. 1 in reference 13 and the documentation for the various data is given there. In addition, Fig. 22 includes new data, largely from this laboratory, which brings it up to date.

The points corresponding to the nuclides characterized in the present research are especially designated in Fig. 22 in order to emphasize the manner in which they contribute to the systematics. The data also make an important contribution to the study of the relationship between half-life and alpha-energy, but the curves showing this are not reproduced here, since several are required owing to dependence on the mass number types. Plots showing this relationship for even-even isotopes define for each element regular lines which are close to the curves calculated by selecting a reasonable function for nuclear radius; on the other hand, the nuclei with odd nucleons invariably depart from these curves in the direction which corresponds to prohibition of alpha-decay (reference 13).

It is of interest to predict the radioactive properties of the still undiscovered nuclides which are even more neutron deficient than those studied here. Thus, we can see from extrapolation of the curve corresponding to uranium in Fig. 22 that we might expect an alpha-disintegration energy of some 7.0 to 7.2 Mev for U^{227}. This corresponds to an alpha-emission half-life for this nucleus of the order of a minute, including in the prediction a small factor for the prohibition which should be introduced because of its even-odd character. Since the half-life for orbital electron capture by U^{227} should be substantially longer than this, and since, similarly, the K/α ratio should be small for its daughters, the U^{227} series should decay mainly as follows:

$$U^{227} \xrightarrow{\alpha} Th^{223} \xrightarrow{\alpha} Ra^{219} \xrightarrow{\alpha} Em^{215} \xrightarrow{\alpha} Po^{211}\,(AcC') \xrightarrow{\alpha} Pb^{207}\text{ (stable).}$$

In a similar manner to that used for U^{227}, the alpha-disintegration energies and half-lives for the daughter isotopes can be predicted; and such considerations lead to the conclusion that these should be about as follows: Th^{223}, 7.5–7.7 Mev, 10^{-1} sec; Ra^{219}, 7.9–8.1 Mev, 10^{-3} sec; Em^{215}, 8.6–8.8 Mev, 10^{-6} sec.

Similar considerations with respect to Pa^{225} lead to the prediction of an alpha-disintegration energy of some 7.2 to 7.4 and a half-life of perhaps 10 sec. The daughters (Ac^{221}, Fr^{217}, At^{213}) in the alpha-emitting decay chain would have increasing alpha-energies and decreasing half-lives in a manner similar, but, of course, different in detail to the above discussed U^{227} series. The prediction of half-lives is less certain here owing to the odd-odd character of the members of the Pa^{225} series and, hence, the greater and somewhat unpredictable degree of prohibition.

In addition, there is uncertainty in the alpha-energy to be expected in a nuclide like At^{213} which decays to a nucleus (Bi^{209}) with the stable configuration of 126 neutrons. Similarly, the curves corresponding to the elements of higher atomic number than astatine probably exhibit the same maximum and minimum as those for astatine and the elements below astatine. Thus, nuclides containing 126, or slightly fewer neutrons, should have low alpha-decay energies and hence relatively long half-lives; and this has already been found to be the case for emanation[20, 21] and francium,[21] and also more recently for radium.[22] Observation of corresponding maxima and minima in the curves for the elements higher than radium is a matter of great experimental difficulty because of the problem of producing the nuclides and also because of their relatively short half-lives due to their large neutron deficiency.

Considerations similar to those made for uranium (U^{227}) show that lighter isotopes of elements of atomic number larger than that of uranium (for example, Np^{230}, Pu^{231}, Am^{237}, Cm^{237}, etc.) should have half-lives sufficiently long for observation. A number of these nuclides can, of course, be considered as progenitors of some of the collateral series which are the subject of the present investigation.

No measurements on the radiations accompanying the electron capture process have yet been made on the nuclides in these collateral series which decay by this mechanism in addition to their decay by alpha-emission. The evidence for decay by electron capture comes from the observation of the daughter isotopes which result from this process. The observation and study of the radiations corresponding to electron capture should be possible for a number of these nuclides, for example Pa^{227}, Pa^{228}, Ac^{224}, U^{228}, U^{229}, and Th^{225}. It is interesting to note that the K/α branching ratio seems to decrease with mass number for a given element in the manner which might be expected in view of the much larger variation of alpha-decay rate with energy than is the case for the electron capture process.

It is quite likely, and in fact practically certain, that fine structure in the alpha-particle energies is actually present and has been missed owing to the necessity of measuring the energies in mixtures of alpha-emitters. Further work done more carefully and at higher resolving power should make it possible to observe this. It has become apparent from work done during the last few years that practically all alpha-emitting nuclides exhibit fine structure. The amount of this seems to be greatest, on the average, for the odd-odd species, less for the even-odd and the odd-even, and least for the even-even species. It should be noted that some fine structure was observed for the odd-odd nucleus Pa^{228}; and it is certainly to be expected that it should be especially apparent in its daughter nuclei Ac^{224}, Fr^{220}, and At^{216}.

The predominantly alpha-emitting nuclei Pa^{227} and U^{229}, formed by reactions such as $Th^{232}(p, 6n)Pa^{227}$, $Th^{232}(d, 7n)Pa^{227}$, and $Th^{232}(\alpha, 7n)U^{229}$ are especially suitable for the study of the excitation functions corresponding to these interesting reactions for their production. This has been the subject of another investigation.[14]

We wish to thank James T. Vale and the crew of the 184-inch cyclotron for their assistance in carrying out this work.

APPENDIX

In this research a variety of techniques had to be employed in order to measure the radioactive properties of the isotopes whose half-lives range from days to microseconds. These techniques range from laborious chemical separations of one element from all other elements to electronic methods for measuring short times between two successive alpha-pulses.

For isotopes with half-lives of a day or so, chemical procedures ensure complete separation from even small quantities of contaminating activities. If, on the other hand, the desired isotope has a half-life of less than an hour, the requirement of purity must be made consistent with the requirement for speed of chemical separation and purification. In general, physical methods must be relied upon to measure and identify isotopes of half-lives of less than a minute. Counting techniques must also be geared to the half-life of the substance upon which the measurements are to be made.

A. Types of Bombardments

In order to obtain the maximum yields in the present work, the internal beam of the cyclotron was used, except when other arrangements could meet a special need (with consequent lowering of yield). The internal beam usually gives about 1 μamp of deuteron and proton current and about one-tenth of this for helium ions.

In general, foils of thorium metal were bombarded either for a time about equal to the half-life of the activity desired or until a sufficient amount of that activity had been produced. The target

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[20] Ghiorso, Meinke, and Seaborg, Phys. Rev. 76, 1414 (1949).

[21] Hyde, Ghiorso, and Seaborg, Phys. Rev. 77, 765 (1950).

[22] E. K. Hyde and F. F. Momyer (unpublished work, 1950).

foils, measuring about 1.5 by 0.5 inches, were clamped into a holder which could be mounted on the "probe" target of the cyclotron and inserted into the tank to intercept the beam. The energy of the particles which struck the target was determined by the radius at which the leading edge of the target foils were set.

In the first bombardments several 5-mil foils were stacked on each other to increase the reaction yields. Later, however, after it had been found that the ion beam penetrated only a few millimeters back from the leading edge of the target, a target holder was designed in which a target could be bombarded on edge. This holder is put on the end of the 184-inch cyclotron probe in such a way that it requires the beam to traverse the width of the thorium foil instead of its thickness. Hence, for the same weight of target material in foil form, a factor increase of at least ten in yield could be obtained by using this target holder. It was only by the application of this concept of bombarding a target "on edge" that it was possible to obtain sufficient yield in many reactions to obtain the required data.

When the isotopes with long half-lives were being studied, pieces of thorium of 25-mil thickness were used to increase the total yield of the protactinium or uranium. When the time for chemical separation was short, however, thinner pieces of thorium, 5 mils or less in thickness, were used to ensure rapid dissolving.

In some cases, thorium nitrate powder wrapped in aluminum foil was used as the target in order to reduce further the time for dissolution of the target. These bombardments in the vacuum chamber were difficult, however, since often the salt outgassed too much and prevented the attainment of a vacuum sufficiently high to proceed with the bombardment.

B. The "Jiffy Probe"

When it is necessary to decrease the time between the end of the cyclotron bombardment and examination of a sample, use is made of the so-called "jiffy probe." This probe, a long hollow tube with a thin concave aluminum end-window, can be inserted into the tank of the cyclotron. The inside of this tube is kept at atmospheric pressure; hence, the window must be strong enough to withstand the vacuum of the tank. A "rabbit" holding a target is blown by compressed air to a position at the end of the tube as close as possible to the window. At the end of bombardment, the target is blown out through the end of the probe tube with compressed air. Provision is made in the rabbit to hold either a metal target on edge or a small cylinder containing a salt of the element to be bombarded. In the bombardment, the beam current hitting the target is reduced by a factor of at least ten from that attained with the internal beam.

After bombardments of the order of a minute were made with the jiffy probe set-up, the doors of the cyclotron were opened immediately and the target blown out of the probe into a lead carrier. This carrier was then taken to a truck and the combined solution and extraction of the product from the target was made while the truck was being driven some 100 yards to the chemistry building. There the sample was evaporated on platinum and placed in the differential alpha-pulse analyzer by means of a fast sample changing mechanism. This method took a minimum of 3.3 min from cyclotron shutdown to the beginning of the first alpha-pulse analysis for the isolation of protactinium and 4.5 min for the isolation of uranium.

C. Target Chemistry

The thorium targets were very radioactive when removed from the internal beam of the 184-inch cyclotron. Although much of this activity comes from fission products of the thorium which are present in good yield, there is also appreciable radioactivity owing to high yield spallation products. Hence, the first steps in the chemical separation had to be carried out in such a manner as to avoid overexposure to the radiation.

Since the protactinium half-lives vary from a day to minutes, the chemical procedure varied from bombardment to bombardment. For the experiments in which Pa^{227} or Pa^{226} were studied, a single extraction with a solution of $0.4M$ thenoyltrifluoroacetone (TTA)[14] in benzene was sufficient to separate these isotopes from all other alpha-emitters. Zirconium, hafnium, and probably some niobium and iodine fission products are also extracted; but these are all beta-emitting activities and do not affect the alpha-counting. In order to obtain good resolution in pulse analyses of certain protactinium samples with a low intensity of alpha-activity compared to the beta-activity, it was necessary to separate the protactinium from the beta-emitting activities through the use of a further extraction of the protactinium into di-isopropyl ketone.

In general, the chemical procedure for the isolation of Pa^{227} involved solution of the thorium metal in concentrated nitric acid to which a few drops of $0.2M$ ammonium fluosilicate had been added to accelerate this process. This solution was diluted to about $4N$ acid and contacted with an equal volume of TTA-benzene solution. The phases were separated and aliquots of the organic layer containing the protactinium were evaporated on platinum.

A more complicated procedure was used for the isolation of the longer-lived protactinium isotopes. This procedure involved carrying of the protactinium on manganese dioxide, dissolution of this precipitate through the use of hydroxylamine solution and a second co-precipitation on manganese dioxide when needed to reduce the volume; this was followed by extraction of the protactinium into di-isopropyl ketone from acid solution and washing of the ketone layer with water in order to separate small amounts of fission products which might have come through; and finally, extraction of the protactinium into $0.4M$ TTA in benzene solution and the evaporation and flaming of this solution on a platinum plate to give an essentially weightless sample. The co-precipitations with manganese dioxide are instrumental in removing to a very high degree all of the other radioactivities. For the characterization of the Pa^{228} series, however, it was usually necessary to eliminate only the zirconium and niobium fission products through the use of the di-isopropyl ketone extraction procedure which, when combined with the TTA-benzene extraction procedure, provided enough purity for accurate results from the counting of alpha-particles.

For the uranium alpha-emitters, the procedure used by Newton[23] involving ether extraction of the uranium from $10N$ ammonium nitrate solutions was used. Another procedure developed by Crane[8] leads to higher purity uranium fractions, but it was found satisfactory for the present experiments to extract only with ether and wash the ether with several portions of saturated ammonium nitrate solutions before finally re-extracting into water and evaporating the samples on platinum plates.

For the experiments in which the jiffy probe was used with thorium nitrate targets, the salt was dissolved directly in a mixture of the aqueous medium and the organic extracting agent, so that the stirring for dissolution also served as the stirring for extraction.

D. Separation of Daughter Activities

1. *Chemical Separation*

The usual procedure for separating daughter radioactivities, applicable when the half-lives of the daughters are sufficiently long, is to perform actual chemical separations.[8] Wherever possible in the present work, the daughters were chemically separated in order to definitely prove their atomic number.

Protactinium daughters of uranium isotopes were separated by the TTA-benzene extraction procedures, which were essentially the same as those used for separations from target materials.

Thorium fractions were separated by co-precipitation with zirconium phosphate precipitates, which are quite specific for carrying thorium to the exclusion of other elements in this region. Since this phosphate precipitate is much too bulky to be suitable for pulse analysis experiments, it was metathesized first to the fluoride (using lanthanum fluoride as carrier for the thorium) and then to lanthanum hydroxide, which was finally dissolved in

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[23] A. S. Newton, Phys. Rev. 75, 209 (1949).

hydrochloric acid and evaporated as lanthanum chloride containing the thorium activity.

Actinium was separated in several cycles in which it was carried by lanthanum fluoride, metathesized to lanthanum hydroxide, and redissolved in acid. The solution from which the lanthanum fluoride was precipitated contained barium as "holdback" carrier for radium. Thorium was specifically removed in this procedure by co-precipitation on zirconium phosphate which was removed as a "by-product" precipitate.

Bismuth was separated by co-precipitations on lead sulfide, the precipitate being dissolved in hot concentrated hydrochloric acid and then reprecipitated. The lead was finally separated from the bismuth by precipitation as lead sulfate.

2. *Separations by Volatilization*

Several elements in the heavy region are quite volatile. Hence, in the present work it was possible to remove emanation isotopes by merely heating in a flame a platinum plate containing a series of alpha-emitters. Francium, astatine, and polonium can similarly be at least partially volatilized by "flaming" such a plate. In none of the studies was it necessary to collect the above elements directly after the flaming operation. Instead, the indirect effect of the growth of daughters in the remaining sample was measured as the isotope that had been removed by volatilization grew back into equilibrium with its parent.

3. *Recoil Separations*

A third and very useful method of separating daughters from the parent activities takes advantage of the recoil imparted to the daughter atom when the parent emits an alpha-particle. When an electric field is imposed between a plate containing the sample and another plate, these recoiling daughter atoms can be collected on the second plate when it is negatively charged. This collector plate, then, is free from the first member of the series present on the original plate, although there may be present on it varying amounts of subsequent members of the series. Similarly, if a second-order recoil transfer is made, in which a further recoil fraction is collected from the first recoil collection plate, neither the first nor second members of the series can be present. This procedure can be extended to third-order or triple recoils, etc., if sufficient activity is available initially. The yield of this type of recoil collection is about 10 percent; higher yields (i.e., up to nearly 50 percent) can be obtained in vacuum without the necessity of an electric field.

An adaptation of this method has made possible half-life determinations on isotopes with values ranging from 30 sec to about 20 msec. Basically, the apparatus consists of a 13-inch diameter rotating metal disk which is wired electrically to act as the collector for recoiling atoms, a sample holder which positions the sample face down over the outer rim of the disk, and an alpha-counting chamber which can also be positioned above the outer rim of the disk. The disk is rotated under the parent sample at a known speed. Recoiling daughter activities are collected along the rim of the disk and the alpha-particles from these activities are counted through the slit window of the alpha-particle counting chamber. By changing the angle between the sample and the chamber, counts of different intensities are registered. The activity obtained at a certain angle is plotted as one coordinate and the angle as the other; thus, the usual type of logarithmic curve can be obtained from which the half-life is determined.

E. Counting Apparatus

Alpha-particles were counted in a standard type argon-filled ionization chamber in which the pulses from electron collection were fed through a fast amplifier and into a scale of 512 counting circuit. Counting losses through coincidence of two or more particles in the chamber for this counting set-up appear to be negligible even at fairly high counting rates.

In order to minimize manual counting operations over long periods of time, an automatic ticker tape recorder was used. This was so arranged that the scaling circuit connected to the alpha-particle or Geiger counting amplification circuits could actuate a counting mechanism which stamped the count totals on a tape recorder. The stamping times could be set at intervals varying from 0.05 to 64 min. This mechanism made possible half-life determinations in a range not easily available for measurement by ordinary manual recording methods.

When counting of beta- or gamma-rays was required, an end-window alcohol-quenched argon-filled Geiger-Müller tube with a window of 3 mg/cm^2 thickness was used in conjunction with a scale of 64 counting circuit.

F. Alpha-Pulse Analysis

Most of the measurements were made through the use of an argon ionization chamber coupled to a 48-channel differential pulse analyzer.[9] A fast sample-changing mechanism on the ion chamber makes it possible to obtain a great deal of data in a short amount of time. Samples are introduced first into a small air lock which can be evacuated and filled with the same gas as that in the ionization chamber without disturbing the main counting volume of the latter. This arrangement reduces the time required for insertion of a sample into the ionization chamber and the actual start of counting. In addition, it is possible to leave the air lock open when extra speed is required and to rely merely on the flow of argon out of the ionization chamber to prevent air from entering. The resolution of the instrument is understandably poorer in the latter case, but is sufficient for some experiments.

Samples are placed on a turntable which can be turned manually from beneath. With the lock open, the table is free to turn to any position. When closed, however, the lock is sealed against the table, keeping the bulk of the chamber at the required gas pressure, while the lock can be kept at any desired vacuum or pressure.

The pulse analyzer itself has 48 electronic channels, each of which selects and counts all pulses within an adjustable energy range. Since these ranges are continuous, when a plot is made of number of counts per channel against channel number, a histogram is obtained of the alpha-spectrum between two particular predetermined energy values. The energy limits of the 48 channels can be varied electronically to give either a general picture of a wide energy region or a more detailed picture of some of the fine points of the spectrum.

In order to obtain good resolution in pulse analyses of the new collateral decay chains, it was found necessary to collimate the alpha-particles emitted by the samples. The chief purpose of such collimation was to reduce the probability of having parent and short-lived daughter alpha-emissions occur nearly simultaneously in the chamber and record, because of the finite resolving time of the amplifier, as a single large pulse. The amplifier-chamber combination used for these investigations was relatively "slow" so that half-lives as long as 200 μsec would cause a certain amount of this delayed coincidence straggling unless collimation were used. The collimators consisted of sieve-like disks of brass with $\frac{1}{16}$-inch diameter holes and varying thicknesses and were placed directly against the samples. The collimator most often used had a transmission of approximately 10 percent.

The alpha-energies determined with the pulse analyzer were all measured by comparison with those occurring in the natural radioactive series, which in turn have been determined accurately with magnetic alpha-ray spectrographs by several independent investigators. Depending on the ease of resolution for each nuclide, the present measurements have probable errors between 10 and 50 kev.

A few limitations of alpha-pulse analysis should be mentioned here. Since thin, almost weightless plates of samples are required, it is almost mandatory that carrier-free chemical separations be made. Thick samples cause poor resolution of the alpha-particle peaks and often make identification of mixtures of peaks impossible. In addition, there is a limit to the amount of beta-particle activity that can be tolerated before resolution of the alpha-particle peaks is affected. The resolution in the present apparatus is lessened appreciably when the beta- or electron activity reaches the level of from 10^5 to 10^6 counts per minute of low energy radiation. The tolerance for high energy beta-particles is higher.

G. Very Short Half-Life Determinations

As mentioned previously, the rotating disk method can be applied to determinations of half-lives down to about 20 msec. For half-lives shorter than this, an electronic delayed coincidence measuring apparatus has been used. This instrument was designed and constructed by R. Dorr and H. P. Robinson of this laboratory. The time scale of this apparatus is divided electronically into three equal intervals with a counting dial for each interval. One alpha-pulse can trigger the circuit, and if another pulse follows within the first segment of time, it is recorded on the first dial; within the second segment on the second dial, etc. The apparatus is so designed that it can trigger the circuit only for a certain segment of the pulse analyzer spectrum and record only when pulses occur in another segment of the spectrum. In other words, it can be set to trigger on one peak of a series of alpha-particle emitters and record on another. The time scale of the apparatus can be varied and is suitable for half-lives between 50 μsec and 50 msec. Background correction, of course, has to be made for random counts which are not related as parent-daughter.

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Microwave Spectrum of Phosphine, Arsine, and Stibine*

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The microwave spectrum of the mono-deuterated phosphine (PH_2D), arsine (AsH_2D), and stibine (SbH_2D) has been measured. Although a supposedly pure sample of stibine was prepared, phosphine and arsine proved to be major impurities. They were separated from the sample; the microwave spectrometer was used to monitor the distillation process. The quadrupole fine structure associated with the absorption transitions for AsH_2D is used to illustrate the special assumptions which may be made with these molecules having an axis of charge symmetry. These assumptions allow one to rotate the coordinate system from the charge-symmetry axes to the inertial axes without thereby adding unknown cross derivatives to the descriptions of the dyadic ∇E_{zz}. Interpretation of the spectrum of SbH_2D is more complicated. It is not found possible to fit the theory to the observed lines without making use of the second-order perturbations caused by a nearby level of different symmetry but of the same J. This perturbation involves the cross derivatives which had previously been assumed to be zero. With the assumption of cross derivatives approximately one percent of the diagonal terms, the theory fitted experiment within the experimental error. The electric quadrupole interaction in arsine and stibine is thus determined.

In order to measure the electric dipole moment of arsine and stibine, a slight extension is made to the theory of asymmetric tops in a uniform electric field.

The ground-state inversion splitting is determined to be less than 0.5 Mc/sec for all three molecules.

The rotational transitions observed were such that a determination of the structure of these three molecules is made.

I. INTRODUCTION

THE essential problem which forms the topic of this report is that of verifying the spins assigned to the two stable antimony isotopes and of determining the ratio of their quadrupole moments. Antimony forms one of a small group of stable elements[1] (Hg, Xe, Rb, Ir, Sb) in which the addition of two neutrons changes the spin by one unit. All of the spin assignments to these nuclei have been made by means of measurements of the hyperfine structure of optical spectra. None has as yet been verified by microwave spectroscopy, where the resolution available is sufficient to fix the spin of the nucleus without a doubt. Antimony is of interest, furthermore, because of the recent revival of the shell model for nuclei. On the basis of this model, those nuclei which come just after or just before the closing of a shell should have easily predictable electric and mechanical moments. Since antimony falls in the periodic table just after the closing of a proton shell at 50, a precise determination of its properties is of interest to the theories of shell structure.[2–5]

The nuclear information which one obtains from measurements using the techniques of microwave spectroscopy is contained in the fine structure associated with the absorption lines caused by the transition of a molecule from one rotational state to another. Before the nuclear information can be interpreted, the structure of the molecule must be determined. Consequently, any investigation of nuclear properties carries with it, as a by-product, the determination of the structure of the molecule used.

The only known simple molecule containing antimony and possessing the necessary properties of volatility and a permanent electric dipole moment is stibine; its structure, however, was not known. Before the advent of microwave spectroscopy with its discovery of the

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