Radioactive Isotopes of the Rare Earths.
I. Experimental Techniques and Thulium Isotopes

Geoffrey Wilkinson and Harry G. Hicks
Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California
(Received January 19, 1949)

The experimental techniques used in the chemical separation and identification of radioactive isotopes of the rare earth elements are described. The isotopes are produced by bombardment of rare earth oxides with α-particles, deuterons, and protons from the 60-inch Crocker Laboratory cyclotron, and also by bombardment of tantalum with 200 Mev deuterons from the 184-inch cyclotron. The production and properties of three new thulium isotopes are described.

I. INTRODUCTION

THE extreme difficulty in achieving separation of the rare earth elements in a very pure state has been overcome in recent years by two main advances in experimental techniques. These have meant that not only macro, but tracer, amounts of rare earths can be reliably separated from each other in a few hours.

Methods of separation based on multiple oxidation states of the rare earth elements have been developed for europium, samarium, and other rare earths, particularly by McCoy[1] and Marsh,[2] using zinc and sodium amalgam reduction procedures, while the separation of rare earths by the use of columns of ion-exchange resins has been developed in the Manhattan Project, and has been described in a comprehensive series of papers.[3]

These procedures have given a great impetus to research on rare earth isotopes formed in fission of uranium and also by neutron capture.[4] Little work, however, has been done on neutron deficient isotopes formed by proton, deuteron, and α-particle bombardment of the rare earths. A systematic study has, therefore, been undertaken to remedy this deficiency in the knowledge of such isotopes, and further, to allow interpretation of the results of high energy particle bombardments of elements above the rare earths using the 184-inch cyclotron. In a previous note,[5] a list of new rare earth activities and their properties was given; the present paper describes the experimental procedures used, and the properties of the new thulium activities.

[1] H. N. McCoy, J. Am. Chem. Soc. **57**, 1756 (1935); **59**, 1131 (1937); **63**, 3422 (1941).
[2] J. K. Marsh, J. Chem. Soc. 398, 523 (1942).
[3] E. R. Tompkins, J. X. Khym and W. E. Cohn, J. Am. Chem. Soc. **69**, 2769 (1947); F. H. Spedding *et al.*, J. Am. Chem. Soc. **69**, 2777, 2786, 2812 (1947); E. R. Tompkins and S. W. Mayer, J. Am. Chem. Soc. **69**, 2859, 2866 (1947).
[4] E. R. Tompkins, J. X. Khym and W. E. Cohn, J. Am. Chem Soc. **69**, 2769 (1947); J. A. Marinsky, L. E. Glendenin, and C. D. Coryell, J. Am. Chem. Soc. **69**, 2781 (1947); D. H. Harris and E. R. Tompkins, J. Am. Chem. Soc. **69**, 2792 (1947); B. H. Ketelle and G. E. Boyd, J. Am. Chem. Soc. **69**, 2800 (1947); W. E. Cohn, G. W. Parker and E. R. Tompkins, Nucleonics **3**, 22 (1948).
[5] G. Wilkinson and H. G. Hicks, Phys. Rev. **74**, 1733 (1948).

II. EXPERIMENTAL

A. Bombardments

Where comparatively large quantities of material were available, hundred milligram amounts of rare earth oxide were spread on a ridged copper target plate, which was then covered with 0.2 mil tantalum foil. In all other cases, ten to twenty milligram samples of the oxides were bombarded on interceptor targets placed in the beam of the 60-inch Crocker Laboratory cyclotron. The finely powdered oxide was spread evenly on a small platinum tray with a grooved inner surface, which was silver soldered to a water-cooled copper holder. The oxide layer was wetted, and a few crops of dilute sodium silicate solution dropped on top of it. After evaporation and drying under an infra-red heat lamp, the oxide was very firmly bound in an even layer. Targets so prepared have withstood over a hundred microampere-hours of 20 Mev deuterons without loss. The targets were covered with 0.2 mil tantalum foil as additional protection.

Bombardments of rare earth oxides have been made with 38 Mev α-particles, 19 Mev deuterons, and 10 Mev protons from the 60-inch Crocker Laboratory cyclotron; runs with low energy α-particles were made by placing suitable thicknesses of tantalum foil over the interceptor target. Tantalum, as the metal foil, was bombarded with 200 Mev deuterons from the 184-inch cyclotron.

B. Chemical Separations

After bombardment, the rare earth oxide was dissolved in nitric acid, and insoluble matter removed by centrifugation. Carriers for contaminating activities likely to be formed from the target materials—copper, tantalum, platinum, sodium silicate, etc.—were added, and the rare earth fluoride precipitated from hot $2N$ nitric acid solution by addition of hydrofluoric acid. The washed fluoride was dissolved in a mixture of concentrated nitric acid and saturated boric acid; from this solution, the rare earth hydroxide was precipitated by addition of ammonium hydroxide. The washed

hydroxide was dissolved in nitric acid and a further fluoride precipitation made as before. Three or four such cycles were made, after which, the hydroxide was dissolved in a minimum of hydrochloric acid and the solution accurately adjusted to a known volume. Aliquots of this solution were taken for direct measurement of radioactivities, for chemical separation of the individual rare earth elements, and for estimation of the chemical yield of the bombarded oxide. Rare earths were determined for chemical yield measurement, by the precipitation of oxalate, followed by ignition to the oxide, and weighing.

The tantalum, after bombardment with 200 Mev deuterons, was dissolved in the minimum of nitric and hydrofluoric acids. To the boiling solution was added boric acid, to complex the fluoride, followed by cerium III solution as a carrier for the rare earth activities. After dilution, excess hydrofluoric acid was added to precipitate cerium III fluoride. The cerium was purified by hydroxide-fluoride cycles as above. To the final solution in strong nitric acid was added a small quantity of lanthanum (ca. 0.1 mg), and the cerium oxidized to the IV oxidation state by addition of sodium bismuthate. The cerium was then removed by precipitation of cerium IV phosphate from $3N$ nitric acid solution. The lanthanum, with the rare earth activities, was recovered as the fluroide, which was then converted to the chloride for subsequent separations on the ion-exchange columns.

C. Chemical Separation of the Rare Earth Elements

Chemical separation of the individual rare earth elements was made by ion-exchange resin columns, or for europium, by an amalgam reduction method. The principle of column separation involves first the adsorption of the rare earth ions in dilute acid solution on a small quantity of ion-exchange resin. This resin is then placed at the top of a resin column, through which is then passed a solution of a complexing agent for the rare earths, e.g., ammonium citrate. The rare earths are eluted under strictly controlled conditions and pass through the column at various rates; lutecium is the first to appear in the eluate, followed in succession by ytterbium, thulium, erbium, etc.

In preliminary experiments to determine the characteristics of column separations and optimum separation conditions for the rare earths, both inactive rare earths in milligram amounts, and Y^{91} radioactive tracer were used. The former were determined spectroscopically[6] and the Y^{91} determined by its radioactivity.

[6] Spectroscopic analyses of the rare earths were made in this laboratory by Mr. J. Conway and Mr. M. Moore, to whom we are greatly indebted for their assistance.

Table I. Production and properties of thulium isotopes.

Isotope	Decay	Half-life	Energy of radiation in Mev Particles	Energy of radiation in Mev γ-rays	Produced by
Tm[166]	$K\beta^+e^-\gamma$	7.7±0.1 hrs.	2.1 (β^+) / 0.24, ~1 (e^-)	L, K x-rays / 1.7	Ho-α-3n / Er-p-n
Tm[167]	$Ke^-\gamma$	9.6±0.1 days	0.21 (e^-)	L, K x-rays / 0.22, 0.95	Ho-α-2n / Er-p-n / Ta-d-5z, 16a
Tm[168]	$Ke^-\gamma$ (β^-?)	85±2 days	0.16, 0.5 (e^-)	L, K x-rays / 0.21, 0.85	Ho-α-n / Er-p-n / Tm-n-2n

1. *Preparation of the Column.*—All column separations were made using Dowex-50,[7] an aromatic hydrocarbon polymer containing many nuclear sulfonic acid groups. The resin used was the colloidal agglomerates, Batch 19891M supplied as the sodium form. The ammonium form of the resin was prepared by stirring with saturated ammonium chloride solution; excess ammonium chloride was removed by washing with water. The resin was graded to have a settling time of less than five minutes for five centimeters in water at room temperature. The length of the preliminary resin column was 50 cm, with a diameter of 0.4 cm, but in subsequent runs, it was found that 20 cm×0.4 cm and 20 cm×1.0 cm columns gave adequate separation.

2. *Adsorption of Rare Earths on Resin.*—The rare earth solution in hydrochloric acid was adjusted to give a pH between 0.5 and 1.5, the ionic strength being kept at a minimum; this solution was then agitated with about 0.2 ml of resin added in two or three successive portions. The solution and resin were agitated at about 70°C, but were not allowed to stand in contact for more than 15 minutes. This prevents diffusion of ions into the interior of the agglomerates, and subsequent slow elution with poor separations.

3. *Operation of the Column.*—The resin, with the rare earth adsorbed on it, was transferred to the top of the resin column, and the eluting agent passed through. The eluting agent used was a $0.25M$ solution of C.P. citric acid, accurately adjusted to pH 3.05 with ammonium hydroxide. Care was taken to approach this value from the acid side, so that readjustment with acid was not necessary, since it is important for good separations to keep the ionic strength at a minimum. The flow rate was approximately 0.03 milliliter per square centimeter column area per minute; with the columns used, of diameter 0.4 cm, and with a drop size of about 0.03 ml, this flow rate corresponded to one drop in 3.5–4 minutes.

The eluate was collected in 10×75 mm rimless test tubes placed in a perforated turntable, which was rotated automatically at various time settings,

[7] W. C. Bauman, Ind. Eng. Chem. **38**, 46 (1946); W. C. Bauman and J. Eichhorn, J. Am. Chem. Soc. **69**, 2830 (1947).

to place succeeding tubes under the column. Samples were normally collected for 15 minutes. In runs with active materials, aliquots were taken with micropipettes and evaporated on stainless steel disks for counting. Aliquots were also taken for spectroscopic analysis of macro amounts of rare earths present. The amount of rare earth, determined either spectroscopically or by activity measurements, was then plotted against the sample number. This allows estimation of the degree of separation achieved. In all column runs, samples collected before the elution of one "free column volume" were disregarded. After completion of a column run, any residual activity or rare earth was stripped from the column with $0.25M$ ammonium citrate of pH 7 as eluting agent. After thoroughly washing with water, the column was again ready for use.

After separation on the column, the rare earths were recovered by evaporation of the citrate solution with nitric and perchloric acids with subsequent ignition. The rare earth residue was then extracted with nitric acid and the hydroxide precipitated with ammonium hydroxide. If the solution contained only tracer amounts, a small amount of lanthanum was added as a carrier.
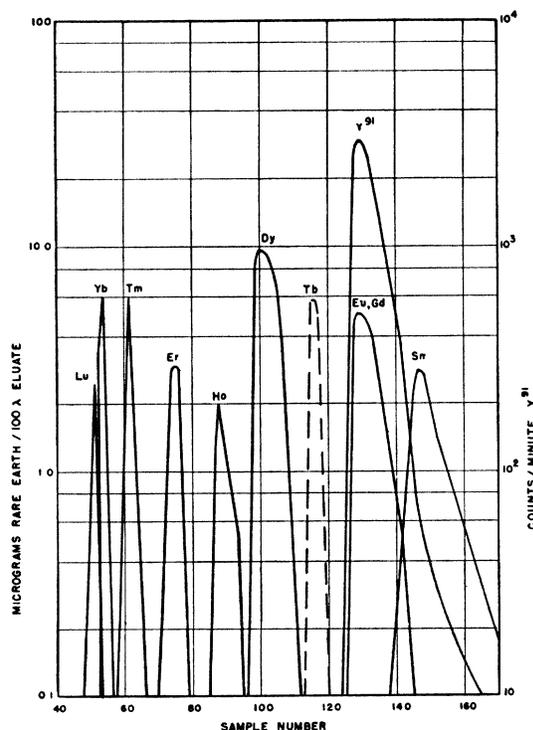
Fig. 1. Standard rare earth elution. 50×0.4 cm Dowex-50 column. Flow rate 0.08 ml/cm²/min. Sampling time 15 minutes; eluate volume in milliliters is 0.282×sample number. Y^{91} was measured by its radioactivity, other rare earths spectroscopically. Terbium is estimated since the cyanogen bands obscure the terbium lines. Eluting agent is citric acid adjusted to pH 3.05 with ammonium hydroxide.

In addition to strict control of the conditions mentioned above, it is also important for successful separations, that the capacity of the resin for adsorption of rare earth ions is not exceeded. For the columns described, the maximum capacity corresponds to approximately 10 mg and 100 mg of rare earth oxide, respectively. Where the starting materials contained significant amounts of other rare earth impurities, and purification was necessary before bombardment, a larger column, which had a capacity for about 1 g rare earth oxide was used. The area of the column and the drop rate were scaled up from the values used in the 0.4 cm and 1.0 cm diameter column runs, the amount of citrate flowing through unit cross-sectional area of resin being kept constant. The progress of any particular inactive rare earth through the column could be checked by using radioactive tracer for a neighboring heavier rare earth. After elution of the active tracer, the sample numbers of the desired inactive rare earth were estimated by comparison with the standard elution curve (Fig. 1). Aliquots of the samples were then examined spectroscopically to allow the pure rare earth fractions to be isolated.

4. *Results in Column Separations.*—In Fig. 1 is shown the "standard elution curve" obtained with inactive materials and Y^{91} tracer. It should be noted that while the lutecium and ytterbium are very close together, samples from the peaks of these curves have no detectable lines of each other or of other rare earths in their spectra. Thus samples of these neighboring elements can be obtained in which the separation factor is at least a thousand.

A typical column run on a bombarded sample is shown in Fig. 2, where the broken line shows the distribution of radioactivity produced by 38 Mev alpha-particle bombardment of holmium oxide. The solid lines show the distribution of inactive carriers of lutecium, ytterbium, erbium, and dysprosium, added as references, and determined spectrographically.

A further example of a column separation is shown in Fig. 3, where the rare earths are present in tracer quantities only. In such cases, separation is generally cleaner and there is less "tailing" of the peaks, than where macro amounts of rare earths are separated. The activities shown in Fig. 3 were spallation products, obtained by the bombardment of tantalum with 200 Mev deuterons from the 184-inch cyclotron. Lanthanum was used as a carrier for the radioisotopes. A study of the radiation characteristics and decays of the peak samples has shown no evidence of contamination.

D. Separation of Europium

Europium has been purified prior to, and recovered after bombardment by a modification of McCoy's method.[1] The europium in $6N$ hydro-

chloric acid solution was reduced to the divalent state by boiling with zinc amalgam. Rare earths other than europium were precipitated by carbonate-free ammonia using cerium as a carrier. After centrifuging, the supernatant solution was withdrawn, the europium oxidized by ozone, and then precipitated by ammonia. The procedure was repeated with both fractions to ensure complete separation.

E. Radioactive Measurements

Measurements were made with "end-on" type Geiger-Müller counters which had 3 mg/cm² mica windows, and were filled with 10 cm argon and 0.5
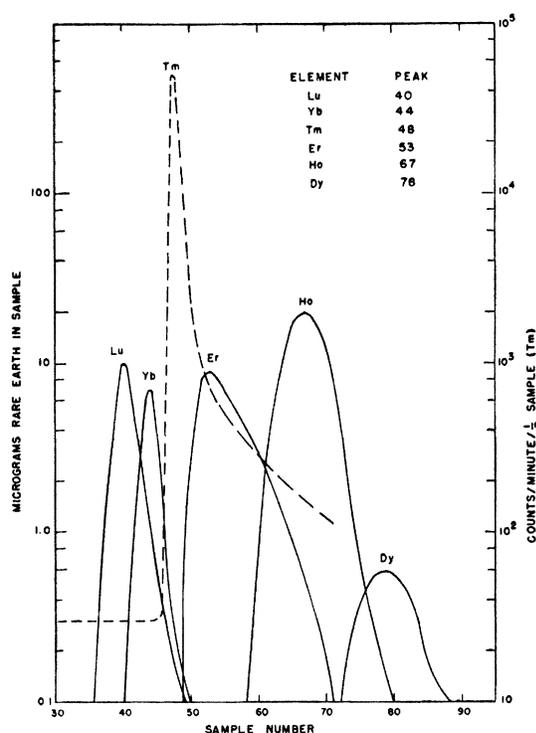
Fig. 2. Column separation of thulium activities from Ho+α bombardment.

cm alcohol; variations in counter efficiency were corrected for by use of a UX₂ reference. A "magnetic counter" was also used, which enabled recognition of positive and negative electrons and provided a check on data obtained from absorption measurements.

Radiation characteristics of active isotopes were determined by beryllium, aluminum, and lead absorption measurements. Electron and soft electromagnetic radiations were resolved by the technique of differential absorption in aluminum and beryllium.[8] The ranges of electrons reported have been taken as the total absorber thickness required for

---

[8] G. Wilkinson, Phys. Rev. **75**, 1019 (1949).
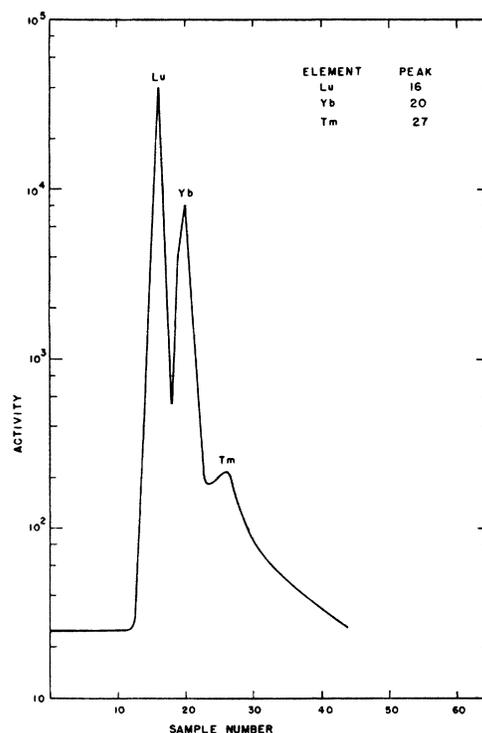
Fig. 3. Column separation of spallation products from 200 Mev deuteron bombardment of tantalum.

removal, i.e., added absorbers plus counter window, air gap, etc. Energies of electrons obtained by aluminum absorption measurements and by the magnetic counter, have been checked using the β^- radiation of P^{32} and the conversion electron of Tc^{99} as references.

In γ-ray absorptions, lead screens up to 45 g/cm² were used, with a beryllium absorber, sufficient to remove all secondary electrons, placed directly below the counter window. Measurements were taken on a counter tube without the usual lead housing, as scattering in the latter has been
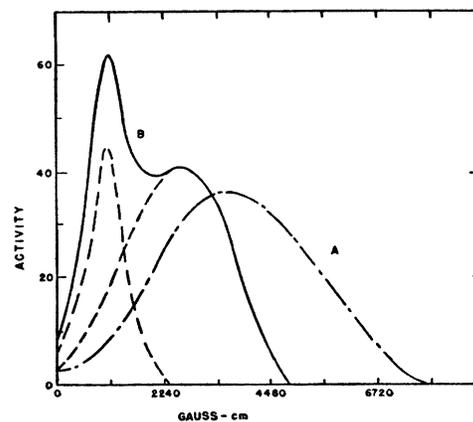
Fig. 4. Magnetic counter distribution of positrons (A) and electrons (B) of 7.7-hour Tm^{166} from Ho+α-bombardment.
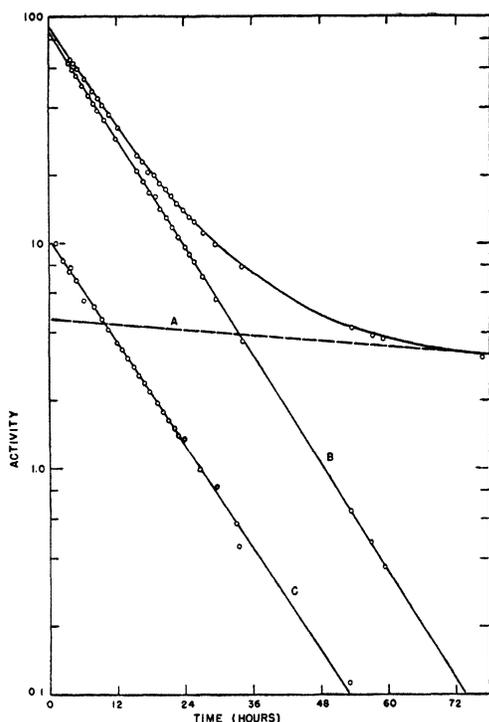
Fig. 5. Decay of 7.7-hour Tm[166]. 9.6-day Tm[167] background (A) and 7.7-hour Tm[166] gross decay from Ho+α. (B) 7.7-hour Tm[166] positron decay (C) from Er+p measured on magnetic counter.

found to give high values for the absorption half-thickness of hard γ-radiation.

Samples for counting were mounted on glass microscope cover slides. Where minimum back-scattering was required, as in measurements of ratios of electrons and electromagnetic radiation, samples were mounted on very thin mica.

For quantitative measurements, the counter geometries were calibrated by use of a weighed uranium (UX₂) standard.

The ratios of the various electron and electromagnetic radiations of the isotopes studied have been calculated in order to allow an estimate of the disintegration schemes, with the object of calculating yields of the isotopes in various reactions. Counting efficiencies of L x-radiation in the counters used were calculated from the absorption in the gas; for γ-radiation from 20 kev to 0.4 Mev a counting efficiency of 0.5 percent was assumed, and 1 percent per Mev thereafter. Corrections were also made for loss of x-rays by the Auger effect. In the region studied, fluorescence yields of 0.8 and 0.5 were assumed for K and L x-radiations, respectively. It is, of course, realized that such ratios, and absolute cross sections, may be in considerable error due to the uncertainties involved. The relative cross sections of the same isotope formed in various

reactions are of more value. Beam intensities were taken from the cyclotron instruments.

III. THULIUM ISOTOPES

In the bombardment of holmium, which has a single isotope Ho[165], with 38 Mev, 30 Mev, and 20 Mev alpha-particles, three radioactive thulium isotopes were produced (see Table I). These were allocated to masses 166, 167, and 168 on the basis of the yields at various energies of the bombarding alpha-particles. The isotopes have been also produced and the mass assignments checked by proton bombardments of erbium. The chemical identity of
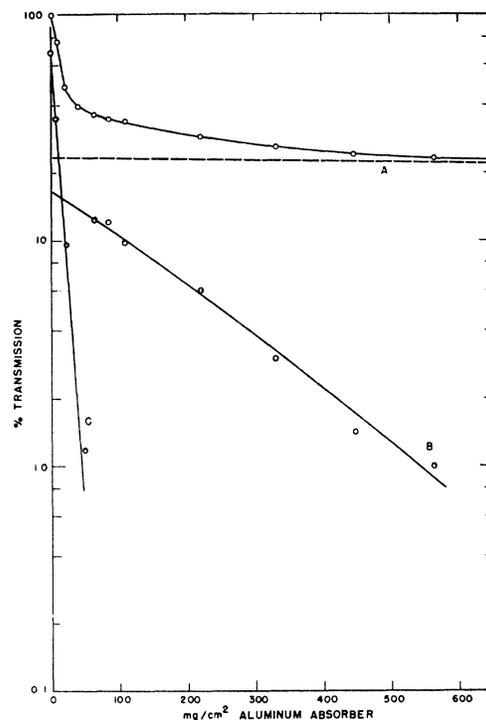
Fig. 6. Aluminium absorption of 7.7-hour Tm[166] from Ho+α. K x-ray and γ-ray background (A), positrons and hard electrons (B), and soft electrons (C).

the isotopes was established by column separations (see Fig. 2).

The holmium oxide used for bombardment was prepared by Dr. J. K. Marsh, Oxford University, England, and was supplied by Johnson, Matthey Company, London, as "Specpure" brand, laboratory number 1031. Analysis showed this oxide to contain about 15 percent dysprosium oxide and about 5 percent yttrium oxide.

The erbium used was Johnson, Matthey and Hilger, "H.S." brand, laboratory number 1755, prepared by Dr. J. K. Marsh. Spectrographic analysis gave ∼0.2 percent yttrium and ytterbium impurities.

Initially the impure oxides were bombarded and the rare earths separated by the column method; in subsequent bombardments the recovered pure rare earths were used.

A. 7.7-hour Tm[166]

The radiations of this isotope consist of positrons, several energies of negative electrons, K x-radiation, and very hard γ-radiation, all of which decay with the same half-life, the best value for which is 7.7 ± 0.1 hours. The gross decay of the isotope produced by 38 Mev alpha-particles on holmium was followed through eight half-lives.

Examination of the isotope on the magnetic counter showed unequivocally that positrons were
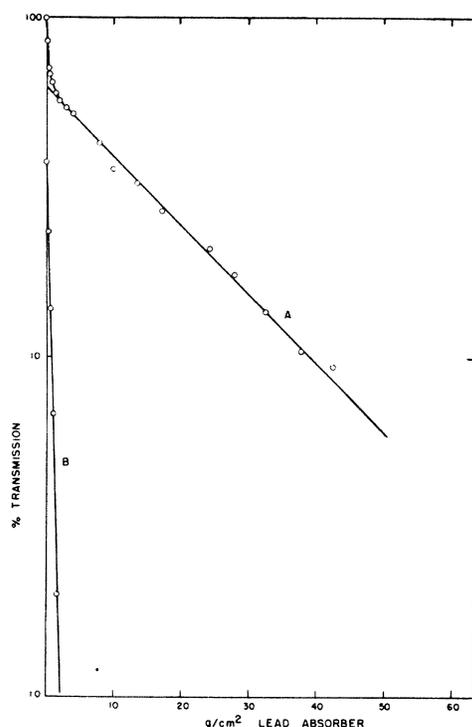
Fig. 7. Lead absorption of 7.7-hour Tm[166] from Ho+α. Hard γ-radiation (A) and K x-rays (B).

present. Figure 4, curve A shows the measured distribution, with end point corresponding to 2.1 Mev maximum energy and with a mean energy of 0.6 Mev. The decay of the positrons (Fig. 5, curve C) was followed on the magnetic counter through six half-lives in both Ho+α and Er+p bombardments.

On the "negative sweep" of the magnetic counter, two groups of negative electrons were observed (Fig. 4, curve B) both of which decayed with the same half-life. While the lower energy peak probably represents a single conversion electron, the second group of harder electrons has a much broader

distribution of energies, and may be a mixture of several conversion electrons which the simple instrument used is incapable of resolving. The maximum energy of this group corresponds to 1 Mev while the average is at $\sim$0.5 Mev.

The aluminum absorption of an infinitely thin sample is shown in Fig. 6. The electromagnetic background was determined after removal of all electrons by a 1400 mg/cm^2 beryllium absorber. No L x-radiation was observed here, although a direct beryllium absorption of the 7.7-hour activity suggests this to be present. The absorption curves show electrons of ranges 70 mg/cm^2 and $\sim$960 mg/cm^2 aluminum, corresponding respectively to 0.24 and 2 Mev; the harder radiation is a complex mixture of positive and negative electrons. Lead absorption of the electromagnetic radiations (Fig. 7), shows two components of half-thicknesses 80 mg/cm^2 and 14.3 ± 0.2 g/cm^2. The energy of the former, 50 kev, agrees well with the value for erbium K x-radiation.

An approximate ratio of positive to negative electrons was obtained by measuring the area under the curves (Fig. 4) from the magnetic counter. The ratio of both the soft and hard groups of electrons to the gross electromagnetic radiation was obtained from aluminum absorption measurements, the usual corrections being made for absorption of electrons is the counter window, etc. From the various measurements, the following ratios, neces-
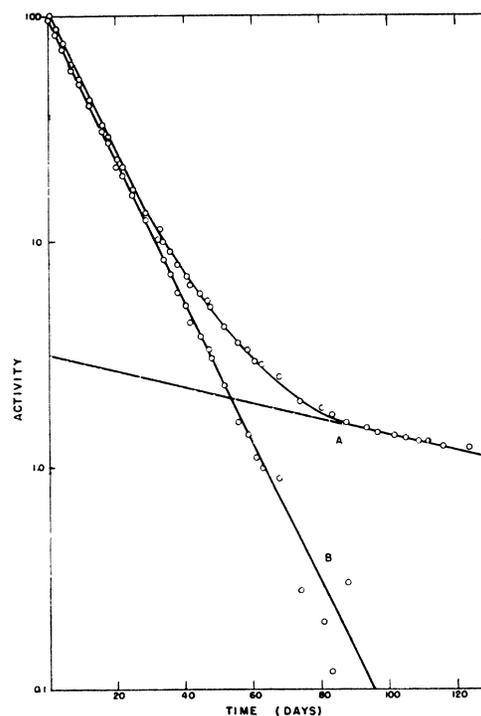
Fig. 8. Decay of 85-day Tm[168] (A) and 9.6-day Tm[167] (B) from Ho+α.

sarily approximate in view of the several corrections and uncertainties involved, were obtained.

$$e_1:e_2:\beta^+:K \text{ x-rays}:\gamma = 0.05:0.003:0.004:1:0.3,$$

where e_1 and e_2 are respectively the soft and hard electron intensities. The very complex radiations can be attributed to orbital electron capture in thulium, leading to excited or metastable levels of the daughter nucleus. Electrons arise from converted γ-ray transitions between the various levels or between these and the ground state. Positron emission may go to an excited level of the daughter nucleus or to the ground state. Since the ratio of electrons to K x-radiation is only ~0.05, approximately 95 percent of the K x-rays measured must arise from orbital electron capture, and it is assumed that 0.95 K quanta represent one disintegration. Thus, the branching ratio for disintegration by positron emission is around 0.5 percent.

It should be noted that the wide distribution of hard negative electrons observed (Fig. 4, curve B) could be due to a continuous β^--spectrum of maximum energy about 1 Mev arising from β^--branching in Tm^{166}, since it is very possible that Yb^{166} is an unreported stable isotope of low abundance. The postulation of stable ytterbium isotope at mass 166 involves no great heresy, since an isotope in such a position would, according to well-known empirical rules of the stability of iso-

topes, be either long lived or stable, and since stable isotopes of erbium, Er^{162},[9] and dysprosium, Dy^{156},[10] which are in analogous positions, are known. A similar situation has arisen with the 16 day Ta^{178},[5] which has been found to decay almost completely by β^--emission, thus implying the existence of an unreported stable isotope of tungsten at mass 178.

If the hard negative electrons of Tm^{166} are, then, a β^--particle spectrum, the disintegration by β^--emission is approximately 0.4 percent of that by orbital electron capture. The branching by β^- and β^+-emission is thus almost the same.

The cross sections for formation of the 7.7-hour isotope were calculated from the intensity of K x-radiation, with the above assumptions for count-
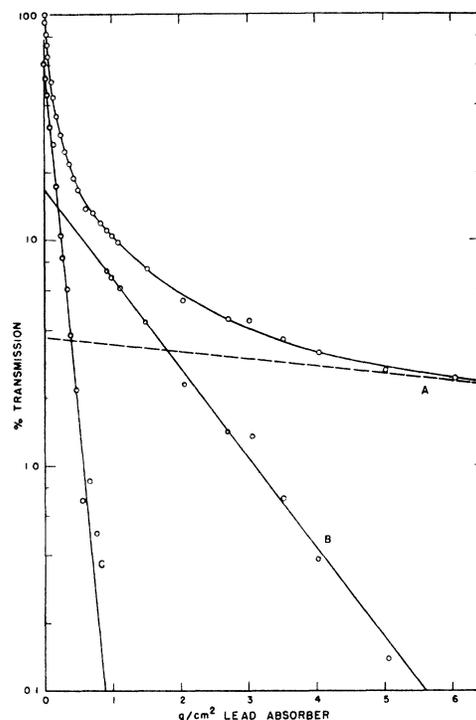
FIG. 10. Lead absorption of 9.6-day Tm^{167} from Ho+α. 0.95 Mev γ-ray (A), 0.22 Mev γ-ray (B) and K x-rays (C).

ing efficiencies and quanta per disintegration. The K x-radiation was measured for weighed samples of unseparated bombarded pure holmium, since no activities other than those of the thulium isotopes were observed. It is possible, however, to determine the specific activity by integrating the counts of the thulium peak in the column separation of a known quantity of bombarded holmium. This method is of general application for calculation of cross sections where activities of two or more elements are present, e.g., in the rare earth fraction of spallation products

FIG. 9. Aluminum absorption of 9.6-day Tm^{167} from Ho+α. K x-ray and γ-ray background (A) electrons (B) and L x-rays (C).

[9] W. Wahl, Finska Kemistsamfundets Medd. 50, 10 (1941).
[10] D. C. Hess, Jr., M. G. Inghram, Phys. Rev. 74, 1724 (1948).

from tantalum with high energy particles, or in deuteron bombardments of rare earths.

B. 9.6-day Tm[167]

After decay of the 7.7-hour isotope from both Ho+α and Er+p bombardments, a residual activity consisting of 9.6-day and long-lived components was observed in the thulium fraction (see Fig. 8). The half-life of the shorter-lived isotope obtained from Ho+α bombardments is 9.6±0.1 days; the gross decay was followed through ten, and γ-radiation, through nine half-lives. The samples were studied on the magnetic counter, no positrons being
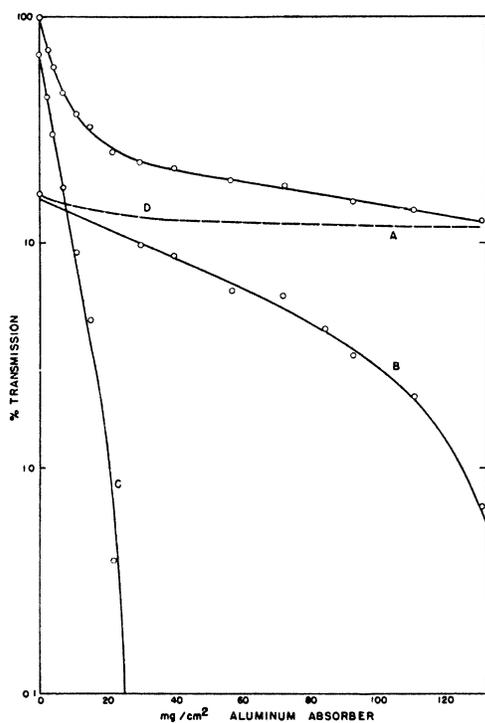
Fig. 11. Aluminum absorption of 85-day Tm[168] from Ho+α. K x-ray and γ-ray background (A), hard electrons (B), soft electrons (C) and L x-rays (D).

observed. The aluminum absorption curve of an infinitely thin, column separated sample of the 9.6-day activity from Ho+α bombardment is shown in Fig. 9. The electrons have a range of 52±2 mg/cm² aluminum, corresponding to 0.21 Mev energy. The electromagnetic radiation consists of four components of half-thicknesses 7.5 mg/cm² aluminum, 80 mg/cm² lead, 770±20 mg/cm² lead and 9.6 g/cm² lead, corresponding, respectively, to energies of 6 kev, 50 kev, 220 kev and 0.95 Mev. The two soft radiations agree well with the energies of erbium L and K x-radiations. The lead absorption curve is shown in Fig. 10.

From absorption measurements, making corrections for absorption of electrons in counter
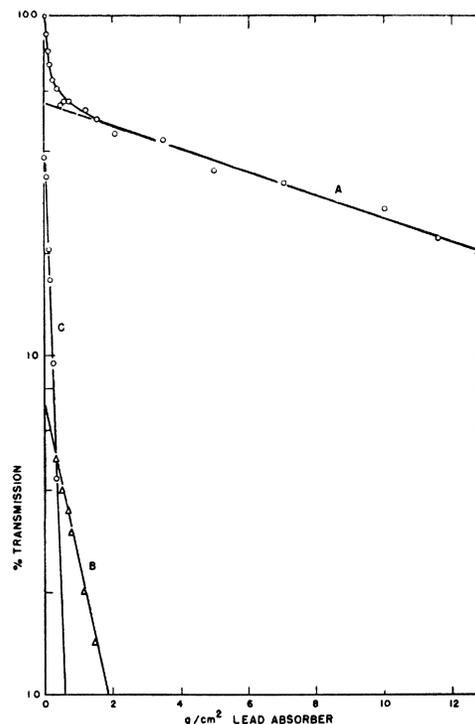
Fig. 12. Lead absorption of 85-day Tm[168] from Ho+α. 0.85 Mev γ-ray (A), 0.21 Mev γ-ray (B) and K x-rays (C).

window, etc., for counting efficiencies of electromagnetic radiation and for loss of x-rays by Auger effect, the following ratios were obtained:

electrons: L x-rays: K x-rays: 220 kev γ: 0.95 Mev γ
$$= 0.3:0.2:1:0.1:0.01.$$

Assuming that K x-radiation arises from production of the conversion electrons, then 0.7 K x-ray quanta probably represent one disintegration by orbital electron capture. This figure has been assumed in the calculation of cross sections for production of the isotope.

The isotope has also been produced by the bombardment of tantalum with 200 Mev deuterons from the 184-inch cyclotron. The measured radiation characteristics were identical with those described above. The reaction producing the isotope is designated Ta-d-5z16a.

C. 85-day Tm[168]

After decay of the 9.6-day isotope, a small residual activity of long-life was found in the column separated thulium fractions from the Ho+α bombardments at 38 Mev. A more active sample was obtained from a 54 microampere-hour bombardment of 80 mg of pure holmium oxide with 19 Mev alpha-particles. The decay of electron and electromagnetic radiations of the isotope have been followed through three half-lives to give a value of

TABLE II. Cross sections in barns for alpha-particle reactions with holmium.

Activity	Energy of α-particles in Mev 38	30	19	Probable reaction	Probable isotope
7.7 hours	1.1	5×10^{-4}	—	Ho-α-3n	Tm^{166}
9.6 days	7×10^{-3}	0.1	10^{-3}	Ho-α-2n	Tm^{167}
85 days	10^{-4}	3×10^{-3}	0.2	Ho-α-n	Tm^{168}

85 ± 2 days. The aluminum absorption curve (Fig. 11) shows electrons of ranges 29 mg/cm^2 (0.16 Mev) and 150 mg/cm^2 (0.5 Mev). The soft electromagnetic radiation corresponding to L x-ray energies was determined after removal of electrons by beryllium. The lead absorption (Fig. 12) of hard radiation shows components of half-thicknesses 77 ± 3 mg/cm^2 (49 kev), ~ 740 mg/cm^2 (0.21 Mev) and 8.8 g/cm^2 (0.85 Mev). The first of these corresponds well with the value for erbium K x-radiation. The ratios obtained for the radiations after the various corrections for counting efficiency, etc. had been made were:

0.16 Mev e^- : 0.5 Mev e^- : L x-rays : K x-rays : 0.21 Mev γ-ray : 0.85 Mev γ-ray

$$= 0.15 : 0.02 : 0.2 : 1 : 0.2 : 0.8.$$

The energy of the soft electrons agrees well with that to be expected for K shell conversion of the 0.21 Mev γ-ray. The conversion coefficient is ~ 0.8. Assuming that K x-rays arise from conversion, then ~ 0.75 of the observed K-radiation may be considered to represent one disintegration by orbital electron capture. The cross sections for production of the isotope have been calculated accordingly. Since the 85-day activity is allocated to Tm^{168}, the possibility of β^- branching exists, and the 0.5 Mev electrons observed may be β^- radiation. With the previous assumptions regarding K x-rays, about 2 percent of the disintegrations would, then, proceed by β^- emission.

The 85-day isotope has been also observed in bombardments of erbium with 10 Mev protons and thulium with fast neutrons. In both cases, the 127-day Tm^{170} is also formed. The latter is reported to have no γ-radiation, and the x- and γ-radiation observed in the thulium fraction decays with a half-life of 85 days. The allocation to mass 168 on the basis of reaction yields is thus confirmed.

D. Discussion

In Table II are given the cross sections for production of the three thulium isotopes by alpha-particle bombardment of holmium at various energies. The absolute values of the cross sections may be in considerable error in view of the several assumptions which had to be made. The relative yields of the isotopes at various energies are significant, however, and allow allocation of the 7.7-hour, 9.6-day, and 85-day activities to masses 166, 167, and 168, respectively, on the basis of α,3n, α,2n, and α,n reactions.

The allocation of the 7.7-hour positron-emitting isotope to Tm^{166} is in agreement with observations that for elements of odd atomic number, only isotopes of even mass number are positron active, and then only when the ratio of neutrons to protons is equal to or less than 1.43.

The yields of the three isotopes in Er+p bombardments are in agreement with the above allocations. Correcting the observed yields for isotopic abundances of the erbium isotopes, the isotopic cross sections for all three cases, assuming p,n reaction, are close to 2×10^{-2} barn. This agrees with the value for the Lu-p-n reaction previously reported.[11]

No evidence of thulium activities with half-lives shorter than those reported was seen in Ho+α, Er+p, and Tm+n bombardments; an upper limit for the half-life of any shorter-lived isotope, from measurements on non-column-separated materials, is about 15 minutes.

[11] G. Wilkinson and H. G. Hicks, Phys. Rev. 75, 696 (1949).