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Artificial Radioactive Isotopes of Thallium, Lead, and Bismuth

KASIMIR FAJANS AND ADOLF F. VOIGT*
Department of Chemistry, University of Michigan, Ann Arbor, Michigan
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The radioelements produced by deuteron and neutron bombardment of thallium and lead have been investigated. The cloud chamber was used to observe the sign of the particles and the energies were determined from absorption measurements. A low intensity 65-min. lead isotope is formed by the deuteron bombardment of Tl; it emits gamma-rays and electrons of 1.00-Mev energy. The properties of two radioelements reported in a preliminary note have been more thoroughly studied. The long-lived thallium isotope produced by deuteron and neutron bombardment of Tl has a half-life of 3.5±0.5 years; it emits negative beta-particles with a maximum energy of 0.87 Mev. The provisional assignment is to Tl^{206}. The 52-hour Pb isotope from the deuteron bombardment of Tl emits gamma-rays (450 kev), conversion electrons (370 kev), and x-rays (95 kev). Its assignment is uncertain. Two activities first obtained by others from the deuteron bombardment of Pb have been studied. The half-life of the 3-hour Pb was measured as 3.32±0.03 hours and its beta-ray energy as 0.70 Mev. The 6.4-day Bi was found to emit gamma-rays of 1.1 Mev and electrons of 0.86 Mev. The excitation functions for these two activities were measured; that for the 6.4-day Bi indicates that a *d-n* reaction is responsible for its production. The recently reported 10-min. positron activity in Pb and 18-hour Bi activity could not be confirmed.

INTRODUCTION

IN a previous publication[1] we reported part of our study of the activities produced by bombarding thallium with slow and fast neutrons and with deuterons. The present publication reports the continuation of this study and its extension to the activities produced from lead. In the latter work uranium lead with an isotopic composition different from ordinary lead was used in the assignment of mass numbers to the activities. (See the following paper.)

I. SUMMARY OF PREVIOUS INVESTIGATIONS

The early work on thallium was summarized in reference 1 and was concerned with the activation of thallium by slow and fast neutrons to give a 4–5-min. thallium isotope which was assigned by Heyn[2] to Tl^{204}. Low intensities of other activities (50 min. and 97 min.) had also been mentioned.

Deuteron bombardment of lead had been found by Thornton and Cork[3] to give a 3-hour activity which they identified as lead and assigned to Pb^{209}, assuming that its observed beta-decay would lead to stable Bi^{209}. Other lead periods which had been reported were an 80-min. period obtained by DeVries and Diemer[4] from the fast neutron activation of lead and a 1.6-min. period produced by x-ray irradiation by Waldman and Collins.[5]

* Horace H. Rackham Pre-doctoral Fellow, 1940–41.
[1] K. Fajans and A. F. Voigt, Phys. Rev. **58**, 177 (1940).
[2] F. A. Heyn, Nature **139**, 842 (1937).
[3] R. L. Thornton and J. M. Cork, Phys. Rev. **51**, 383 (1937).
[4] H. DeVries and G. Diemer, Physica **6**, 599 (1939).
[5] B. Waldman and G. B. Collins, Phys. Rev. **57**, 338 (1940).

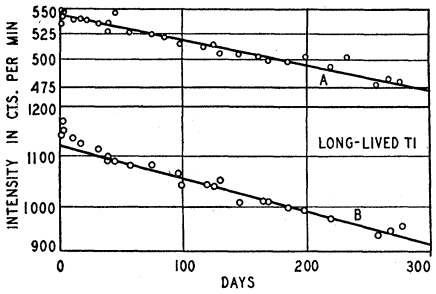

FIG. 1. Decay curves of the long-lived Tl.

In our previous paper[1] we reported a comparison of the artificial 4–5-min. period with AcC″, Tl^{207}. The half-life of the former was measured as 4.23 ± 0.03 min. and the latter as 4.76 ± 0.05 min. The 4.23-min. period was produced in high intensities by the deuteron bombardment of thallium and was identified chemically as Tl. The range of the negative beta-particles which it emits was found to be 0.75 ± 0.05 g/cm^2, which leads to an energy of 1.65 Mev if the Feather formula is used. It does not emit gamma-rays.

Prolonged slow neutron activation did not give the 97-min. period previously reported but did yield a low intensity of a new long period which was found in greater intensity from the deuteron bombardment of thallium. Its half-life appeared to be between 1 and 2 years and it was provisionally assigned to Tl^{206}.

An activity of 52 hours half-life was produced by the deuteron bombardment of Tl. It was identified chemically as lead and found to emit electrons and gamma-rays.

Since that time Bretscher and Cook[6] reported the production of a 4.6-min. Tl activity by the fast neutron activation of lead. They concluded it to be AcC″, Tl^{207}, by comparing its half-life with those of AcC″ from actinium, 4.7 min., and of the slow neutron-induced Tl activity, 4.1 min.

A thorough study of the activities produced in Tl and in Pb was made by Krishnan and Nahum[7] who mention our previous publication in a note added in proof. They reported 4.4 ± 0.1 min. as the half-life of Tl^{204}, and their absorption measurements led to a range of 0.8 g/cm^2 of aluminum for the beta-particles. They found fast neutron activation of thallium to give a 13-day period which is also produced by the action of deuterons on mercury, and they assigned it to Tl^{202}.

They reported two lead isotopes produced by the deuteron bombardment of Tl. One was a 54-hour activity emitting gamma-rays, electrons and x-rays, which is obviously identical with our 52-hour period. The other was a 10.25-min. positron activity.

From the deuteron bombardment of lead they observed three periods: the 3-hour lead isotope, a 6.35-day Bi activity emitting gamma-rays, electrons and x-rays, and a weak 18-hour activity found in the Bi fraction.

II. Experimental Methods

1. Production and measurement of the radioactivity

The activities were obtained on the cyclotron of the Physics Department of this University which has been producing a beam current of 5–15 μa of 9–10-Mev deuterons. The measuring instruments were two Lauritsen quartz fiber electroscopes, equipped with cubical ionization chambers which have been used for some time in this laboratory and recently were made of cast aluminum as designed by Mr. A. S. Micelli. They are 8 cm on an outside edge, are provided with thin aluminum windows on the top and bottom, and have glass receptacles filled with anhydrous magnesium perchlorate as a drying agent. These electroscopes were used mostly for the work with short periods while several bubble-type Geiger-Mueller tubes with scaling circuits served for observing the longer periods. Absorption curve measurements were made with both types of instruments.

2. Purification of the material

The extensive purification of the thallium used for the bombardments has been described previously.[1] To obtain lead free from thallium, reagent quality lead nitrate was acidified with HCl, boiled to oxidize any thallium present, and treated with ether to extract it. The lead was precipitated as carbonate, ignited to PbO, and bombarded as such or as PbO_2 obtained by passing chlorine into an alkaline solution of the PbO.

[6] E. Bretscher and L. G. Cook, Nature **146**, 430 (1940).
[7] R. S. Krishnan and E. A. Nahum, Proc. Cambridge Phil. Soc. **36**, 490 (1940).

3. Chemical processes used in the separations

After the bombardment of thallium (as metal or Tl_2O_3) and its dissolution in acid, the following process was generally used to separate the thallium and lead from each other and from any impurities:

(a) precipitation of Pb as $PbSO_4$;
(b) precipitation of Hg, etc., as sulfides in acid solution;
(c) oxidation of thallium to $TlCl_3$, followed by its extraction with ether;
(d) reduction of $TlCl_3$ to TlCl;[8]
(e) precipitation of thallium as TlCl, TlI, or Tl_2CrO_4;
(f) purification of the lead fraction (a) by dissolving it in ammonium acetate and reprecipitating it with sulfuric acid.

Whenever necessary the chemical identities were proved by fractional crystallization (on cooling) of the carriers of the activity, TlCl and PbI_2. The fractions obtained were weighed and measured and the specific activities were compared.

After bombarding and dissolving the PbO or PbO_2, steps (a) and (f) (see above) were used for obtaining the lead isotopes while the bismuth was separated by one of the following reactions:

(a) precipitation as Bi_2S_3 from an acid or ammonium polysulfide solution;
(b) reduction to metal in alkaline solution by sodium stannite or formaldehyde.

For further purification the Bi_2S_3 or Bi were converted to $BiCl_3$, and BiOCl was precipitated by dilution of a slightly acid solution of the latter. For final chemical identification the fractional precipitation of BiOCl on dilution was used.

III. Activities Studied

1. The long period in thallium

Two samples containing relatively high intensities of the long period thallium were obtained by deuteron bombardments of 37 and 100 μah at 9 Mev. Their intensities were 500 and 1100 ct./min., respectively. The half-lives resulting from the curves A and B in Fig. 1 are 4.0 ± 0.5 and 3.1 ± 0.4 years, the average value is 3.5 ± 0.5 years.

The chemical identification as thallium was made as described above. The specific activity of three TlCl fractions agreed within 5 percent.

Cloud-chamber photographs show the beta-radiation to be negative and absorption measurements indicate the absence of gamma-rays. The absorption curve of the beta-rays of the thallium and of RaE were measured on the same instrument, and the range for thallium was obtained by using the comparison method of Feather.[9] The range found (see Fig. 2) was 0.31 ± 0.03 g/cm^2 of aluminum, which leads to an energy of 0.87 ± 0.05 Mev, if the Feather formula is used, $R=0.543E-0.160$.

Periods of the same order of magnitude but of low intensity were obtained by slow neutron activation (6 ct./min.) and Cd-filtered fast neutrons (1–2 ct./min.).

Thus fast as well as slow neutron bombardment apparently produces both thallium periods, the 4 min. (see Sec. I) and the 3 yr. The two possibilities for their assignment are Tl^{204} and Tl^{206}.[10] One would expect that the isotope 204

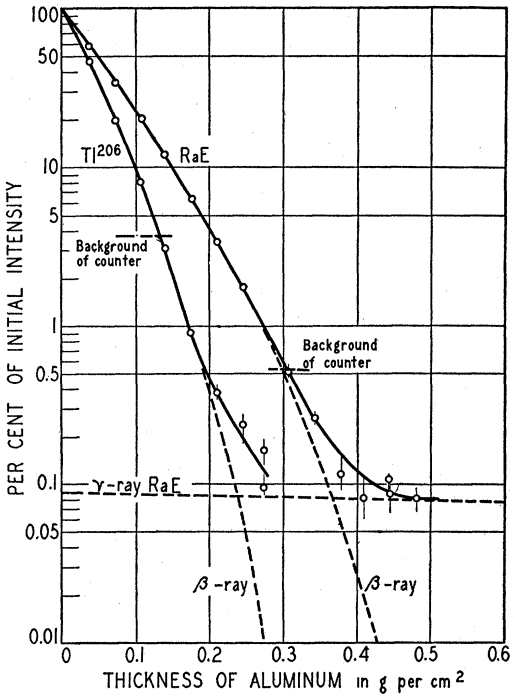

FIG. 2. Absorption curves of the long-lived ∫Tl and RaE.

[8] If a more rapid separation was desired, steps (c) and (d) were omitted.

[9] N. Feather, Proc. Camb. Phil. Soc. **34**, 599 (1938).

[10] The possibility of isomerism has not been overlooked, but is improbable, because of the type of activities, both being beta-emitters with no gamma-rays.

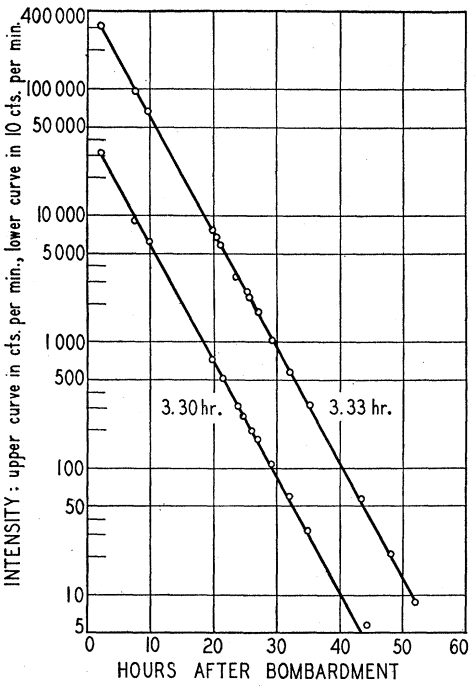

FIG. 3. Decay curves of Pb^{209}.

would be produced in good yields from 203 by slow neutrons and from 205 by fast, while 206 would only be produced by slow neutrons from 205. However, as cadmium filtration does not remove all of the slow neutrons, it is not surprising that some of both activities are found in bombardments with Cd-filtered neutrons, one of these being produced by the slow neutrons not removed by the cadmium. More intense bombardments under controlled conditions will be necessary before a decision can be made. At present it seems best to leave the assignment of the 4-min. period to Tl^{204} and tentatively assign the 3-year period to Tl^{206}.

2. The thirteen-day thallium

We observed this period from fast neutron bombardments of thallium, one of the methods used by Krishnan and Nahum[7] and identified it chemically as thallium by the usual reactions and fractionation process. The average value for the half-life is 11.8 ± 1.2 days, obtained from five rather weak samples.

3. The four-minute thallium

Our work on this activity was reported in reference 1 and is summarized above.

4. Attempts to produce thallium from lead

Lead oxide was given short deuteron bombardments and Tl was separated by the extraction process. The only activity in the thallium was a very weak 10–15-min. period. The intensity was too low for any study to prove the identity of the active material.

5. The fifty-two hour lead

This isotope, produced by the deuteron bombardment of Tl has been studied in more detail than reported previously. In addition to the chemical reactions listed above it was precipitated as PbI_2, $PbCrO_4$, $PbCl_2$, PbS, and PbO_2. The fractional crystallization as PbI_2 gave three samples whose specific activity agreed within 2 percent. Our value for the half-life is 52 ± 0.5 hr.

Absorption measurements of the gamma-radiation in copper and in lead show two distinct radiations, with the following absorption coefficients and energies:

	Mass Abs. Coef.	Energy	Average
Pb	0.30–0.36 cm^2/g	430–475 kev	
	0.93–1.5	(200–250)	
			450±25 kev
Cu	0.077–0.087	425–475	
	0.51–0.57	92–98	

(The conversion was made from tables in the *International Critical Tables* and curves given by Heitler.[11])

Since the energy of the K x-rays from Tl or Pb is about 90 kev, the result for the softer of these two radiations in copper identify it as this x-radiation. The values determined for the energy of this radiation from the data in lead are meaningless because of the discontinuity in the absorption coefficient-energy curve.

The range of the beta-particles in aluminum was found to be 0.110 ± 0.005 g/cm², which, according to a curve given in Rasetti,[12] leads to an energy of 370 kev. Our former value of 500 kev was determined from less accurate measurements and on the basis of the Feather formula which does not apply to energies less than 700 kev.

These data are in complete accord with the picture of the primary activity as a gamma-ray,

[11] W. Heitler, *The Quantum Theory of Radiation* (The Clarendon Press, Oxford, 1936) p. 216.
[12] F. Rasetti, *Elements of Nuclear Physics* (Prentice-Hall, New York, 1936), p. 68.

partially internally converted to give the observed electrons of 370-kev energy which is less than that of the gamma-rays (450 kev) by approximately 90 kev, the binding energy of the K electrons in lead or thallium.

In our previous publication we suggested that this activity was due to a metastable state of either Pb^{204} or Pb^{206}, produced from Tl^{203} or Tl^{205} by the usual d-n reaction, and decaying to the corresponding stable isotope with the emission of the observed gamma-ray. Krishnan and Nahum reported the production of this activity by the slow and fast neutron activation of lead tetraethyl and also found its excitation threshold to be about 7 Mev. These observations led them to the conclusion that the activity is Pb^{205} produced from Tl^{205} by a d-$2n$ reaction and decaying to Tl^{205} by K electron capture. As the discussion of excitation functions (see Sec. IV) seems to indicate that d-$2n$ processes are improbable for heavy elements at these energies, the question is still open.

6. The three-hour lead

A number of determinations of the half-life of this isotope on electroscope and Geiger counter gives the value 3.32 ± 0.03 hr., in considerable disagreement with Krishnan and Nahum's value of 2.75 ± 0.05 hr. In one case our sample was followed for 17 half-lives without showing any other period (see Fig. 3), justifying the conclusion that this is the only long period produced by the deuteron bombardment of lead. Separations were completed in 20 min. so that a short period (less than 5 min.) could be produced and escape detection.

Our value for the range of the beta-particles was 0.22 g/cm² of Al, checking the same value in the experiments of Krishnan and Nahum. The energy corresponding to this range is 700 kev by the Feather formula. The assignment is discussed in the following paper.

7. The one-hour lead

Krishnan and Nahum described a 10-min. positron activity as a lead isotope produced by the deuteron bombardment of a thallium preparation. In order to check this we bombarded pure Tl_2O_3 with a current of 10 μa of 9-Mev deuterons for periods of 5 min. to 1 hour. In each case the separation was made immediately and measurements were begun 15 to 20 min. after bombardment. The results were always the same; there was no trace of a 10-min. period. However, a new weak 65 ± 5-min. period was found in addition to the 52-hour activity (see Fig. 4).

The 65-min. period was identified as lead in the usual way and in particular by a fractional crystallization of PbI_2. Three fractions showed the same ratio of the 1-hour to 52-hour periods within the experimental error. Extrapolated to the end of bombardment these ratios are: 0.36, 0.37, 0.33, agreeing within the uncertainty of ±0.02 for each. The relatively high error is due to the low intensity of the short period compared with that of the longer one. The ratio for infinite bombardment is 1/150 showing that the probability of production of the 65-min. period is much less than that of the 52-hour.

Cloud-chamber observation of the lead precipitate shortly after the bombardment of thallium with deuterons showed only negative tracks. Absorption measurements show gamma- as well as beta-activity, the former being about 17 percent of the total radiation as measured on the Geiger counter.

The absorption curve in Al shows the range of the electrons to be 0.38 ± 0.03 g/cm² correspond-

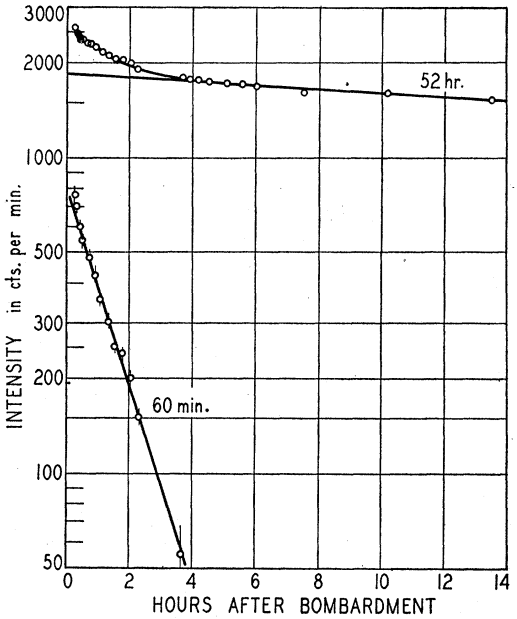

FIG. 4. Decay curves of one hour and 52-hour lead activities.

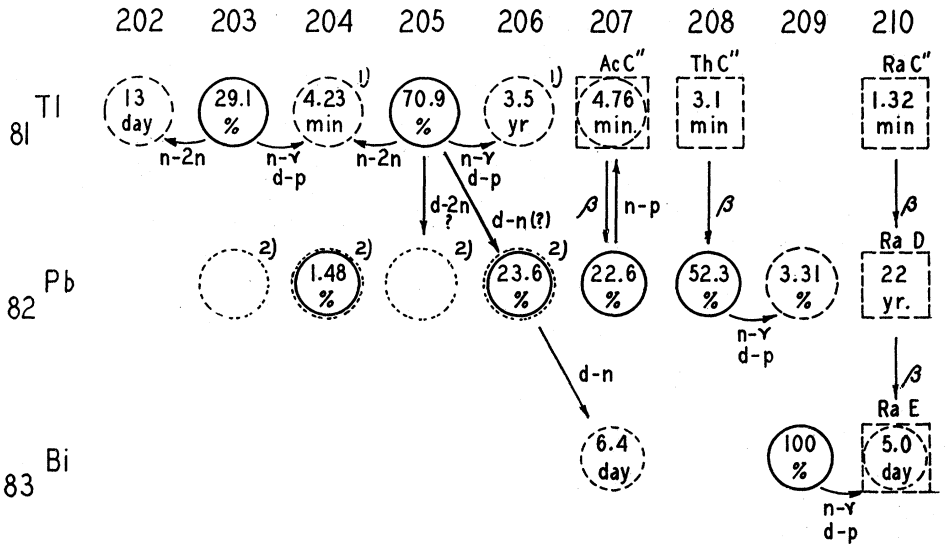

FIG. 5. Isotopes of Tl, Pb, and Bi. Solid circles indicate stable isotopes. Broken squares indicate natural radioactive isotopes. Broken circles indicate artificial radioactive isotopes. Dotted circles indicate uncertain assignments. (1) Assignment possibly reversed. (2) Assignment of 1-hour and 52-hour Pb isotopes is not certain. Pb^{209} has a period of 3.31 hours.

ing to a maximum energy of 1.00 ± 0.05 Mev (Feather). Rough measurements in lead show the energy of the gamma-ray to be of the order of magnitude of a million electron volts. The electron activity may result from the partial internal conversion of this gamma-ray, in which case the energy of the gamma-ray would be 1.1 Mev (see paragraph 5).

The assignment of this activity is still less certain than that of the more intense 52-hour activity. It may be a metastable state of Pb^{204} or Pb^{206} or it may be Pb^{203}, decaying by K capture to Tl^{203}. The latter would require a d-$2n$ reaction for its production, the probability of which is discussed in Section IV.

8. The six-day bismuth

This period was produced by bombarding lead with deuterons and has been identified as bismuth by the method described above. Several determinations of its half-life give the value 6.4 ± 0.1 days in agreement with the value of 6.35 days obtained by Krishnan and Nahum. The range of its beta-rays was measured as 0.30 ± 0.02 g/cm^2 of Al, which leads to an energy of 0.85 ± 0.04 Mev. The absorption coefficient of its gamma-rays in lead was found to be 0.066 ± 0.006 cm^2/g which corresponds to an energy of 1.1 ± 0.1 Mev. If we assume that this isotope emits a gamma-ray which is partially internally converted to give the electrons, we would expect the gamma-ray energy to be 0.95 ± 0.05 Mev. The observed value (1.1) agrees poorly but within the experimental error. The primary decay process is probably K electron capture leading to a stable Pb isotope.

The assignment of this isotope is discussed in the following paper.

The curves show no indication for the weak 18-hour activity found in the bismuth separation by Krishnan and Nahum.

9. Summary

The various stable isotopes and radioactive isotopes, both natural and induced are shown in Fig. 5.

IV. Excitation Functions

The excitation functions of the 3-hour lead and 6-day bismuth isotopes were measured by bombarding a stack of 6 lead foils with deuterons and following the decay of each. The foils were made by rolling reagent quality lead metal to the required thickness, 0.01 to 0.02 mm. They were measured without chemical separation and the 3-hour and 6-day activities were extrapolated to

beginning time for comparison. The thicknesses were evaluated by weighing the measured part of the foils (squares 12 mm on an edge) and determining the area with a comparator. The specific activities are plotted in Fig. 6 against the beam energy. The original beam energy was taken as 9.7 Mev from its range in air, 64 cm (corrected to 760 mm and 15°C). The data of Mano[13] were used to calculate the energy loss of the deuteron beam in Pb. The resulting energy of the beam, calculated for the median thickness of each foil, is used in the curves.

The 3-hour lead, produced by a *d-p* reaction, has an excitation curve similar to those for other *d-p* processes in heavy elements.

In the case of the 6-day Bi a decision is desired as to whether it is produced by a *d-n* or a *d-2n* process. The production threshold is at or above 7 Mev. The threshold for the *d-n* process increases greatly with increasing atomic number. For the lightest elements (Li, Be) it is 0.4 Mev, for those of medium atomic weight it is a few Mev, while for several heavy elements thresholds near 7 Mev have been observed (Hg^{198} from Au^{197}, Po^{210} from Bi^{209}).[14–16]

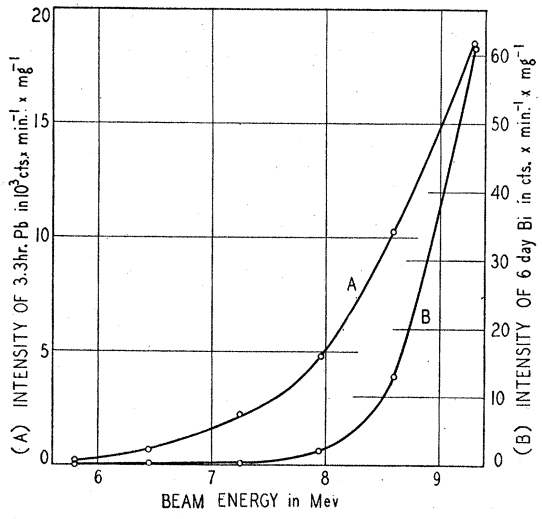

FIG. 6. Excitation curves of the 3-hour Pb and 6-day Bi.

[13] G. Mano, J. de phys. et rad. **5**, 628 (1934).

On the other hand, one excitation curve for a *d-2n* process in the lighter elements (Zn^{63} from Cu^{63})[17] shows a threshold energy of 9 Mev. It is logical to assume that the threshold for *d-2n* processes will also increase with increasing atomic number. For the heaviest elements it would thus be distinctly higher than the value of 7 Mev observed for the Bi activity. The threshold and the shape of the excitation function for Bi resemble so closely those of Hg and Po that it seems probable to assume the same process. As the activity is produced from Pb^{206} (see the following paper) the reaction would be Pb^{206}, *d-n*, Bi^{207}.

This also affects the assignment of the 52-hour lead period. Its threshold has been given by Krishnan and Nahum[7] as about 7 Mev also. Again, this makes a *d-n* process probable and the assignment of the 52-hour activity to a metastable state of Pb^{204} or Pb^{206} more likely than to Pb^{205}. A similar situation may exist with respect to the 65-min. period but the threshold energy of that activity is not known.*

The investigation received helpful support by grants from the Horace H. Rackham Trust Fund.

[14] R. S. Krishnan, Proc. Camb. Phil. Soc. **37**, 186 (1941).

[15] D. G. Hurst, R. Latham, and W. B. Lewis, Proc. Roy. Soc. **A174**, 126 (1940).

[16] H. A. Bethe, Rev. Mod. Phys. **9**, 200 (1937) has concluded on theoretical grounds that the *d-2n* process will become probable at 7 Mev for heavy elements.

[17] R. S. Livingston and B. T. Wright, Phys. Rev. **56**, 656 (1940).

* *Note added in proof.*—The results given in the new paper by R. Sherr, K. T. Bainbridge, and H. H. Anderson, Phys. Rev. **60**, 473 (1941) may influence the discussion in Section IV. They consider it probable that the 25-hour mercury isotope is Hg^{197} rather than Hg^{198}, and, therefore, that its production from Au^{197} is a *d-2n* rather than a *d-n* process.