THE
PHYSICAL REVIEW
A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 63, NOS. 7 AND 8 APRIL 1 AND 15, 1943

Radioactive Isotopes of Mercury

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(Received December 18, 1942)

The radioactive mercury isotopes produced by the bombardment of mercury with neutrons and by the bombardment of gold with deuterons have been studied. Two activities with half-lives of 23 hours and 64 hours, respectively, both decaying by K-electron capture, have been assigned to Hg^{197}, on the basis of critical absorption measurements made on the x-rays emitted. The same method was used to show that the 43-minute activity produced by fast neutrons in mercury belongs to an excited state of a mercury isotope and decays by an isomeric transition to the ground state. A 51.5-day beta-emitter was studied; it is probably to be assigned to Hg^{203}.

IN the present paper, we are reporting in detail the results of studies on radioactive mercury isotopes which we have already published in preliminary form.[1] Most of the bombardments were made with the 14-Mev deuterons of the 60-inch cyclotron and with neutrons produced by the bombardment of beryllium with these 14-Mev deuterons.

PREVIOUS WORK

The first artificially radioactive isotope of mercury was discovered by Anderson[2] in 1936. He reported a half-life period of 40 ± 5 hours induced in mercury by slow neutrons, and he tentatively assigned it to Hg^{205}. Shortly afterward, Pool, Cork, and Thornton[3] reported a 45-minute period produced by fast neutron bombardment of mercury. The authors did not identify the chemical nature of this isotope. Heyn[4] also found a 43-minute period from fast neutron bombardment of mercury and showed that it was due to a mercury isotope. McMillan, Kamen, and Ruben[5] investigated the radiations from this 43-minute activity, and found negative beta-rays with an upper energy limit of 0.42 Mev and gamma-radiation of 70- to 250-kev energy. They assigned this period to Hg^{203}. The same authors also reported a 25-hour activity, weakly induced in mercury by fast neutrons, and chemically identified as mercury.

This was all the work that had been published on artificially radioactive mercury isotopes when the present research was begun in 1940. Shortly afterward, however, Krishnan and Nahum[6] published a paper on deuteron bombardments of some heavy metals, in which they discussed

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[1] C. S. Wu and G. Friedlander, Phys. Rev. **60**, 747 (1941).
[2] E. B. Anderson, Nature **137**, 457 (1936).
[3] M. L. Pool, J. M. Cork, and R. L. Thornton, Phys. Rev. **52**, 239 (1937).
[4] F. A. Heyn, Nature **139**, 842 (1937).
[5] F. M. McMillan, M. Kamen, and S. Ruben, Phys. Rev. **52**, 375 (1937).
[6] R. S. Krishnan and E. A. Nahum, Proc. Camb. Phil. Soc. **36**, 490 (1940).

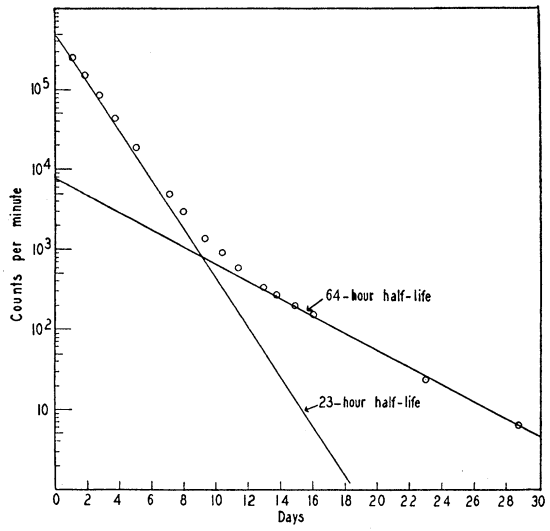

FIG. 1. Decay of Hg^{197} produced by the bombardment of gold with 14-Mev deuterons. The first part of the curve, above 10^4 counts per minute, was measured on an electroscope with thin window (2.5 mg/cm²) which was calibrated against the counter used.

several mercury isotopes: a 48-minute period induced in mercury by fast neutrons as well as by deuterons and assigned to Hg^{197} for reasons which will be discussed later; a 36-hour period produced by fast neutron or deuteron bombardments of mercury and by deuteron bombardment of gold, and assigned to an excited state of Hg^{198} (whose ground state is stable); finally a 5.5-minute period produced in the deuteron bombardment of mercury and assigned to Hg^{205}. Later, Krishnan[7] revised the half-life of the activity assigned by him to Hg^{198*} to 32 hours.

The conflicting assignments of the 43 to 48-minute period[5,6] and particularly the fact that various authors[2,5–7] had reported periods of from 25 to 40-hours' half-life with otherwise very similar properties, led the present authors to make a systematic study of the radioactive mercury isotopes.

Sherr, Bainbridge, and Anderson[8] have recently published results on the transmutation of mercury by fast neutrons, which include a discussion of a 43-minute and a 25-hour activity in mercury. These results are in agreement with ours and will be discussed later in this paper.

CHEMICAL SEPARATIONS

Chemical separations were made after all bombardments. In most of the neutron bombardments of mercury, metallic mercury was used, which was then distilled after the addition of gold and platinum carriers. In a few cases, mercury salts were bombarded; in those cases the mercury fractions were isolated by the precipitation of HgO in the presence of gold carrier.

The deuteron-bombarded gold samples were cut up into small strips; a small amount of mercury was amalgamated with the gold, and the mercury then distilled away from the gold in vacuum. The distillate was mixed with some inactive gold and redistilled. In some cases an alternative procedure was used: The gold was dissolved in aqua regia, a few milligrams each of mercuric chloride and platinic chloride were added, and the solution was evaporated to about 0.5 cc. The residue was taken up in water, and gold and mercury were then extracted with ethyl acetate by the procedure of Noyes and Bray.[9] The separation of gold and mercury was then carried out according to Noyes and Bray. The mercury was finally precipitated in the form of the compound $HgO \cdot HgINH_2$.

Hg^{197}: ISOMERS WITH HALF-LIVES OF 23 HOURS AND 64 HOURS

When mercury was first bombarded with fast neutrons from the Be+D reaction, the decay curve of the mercury fraction was a composite of three half-lives, the shortest one being about 45 minutes, the longest one about 50 days. The intermediate half-life, however, varied between 25 and 45 hours, depending upon the thickness of the sample and that of the window of the measuring instrument. Absorption measurements with aluminum absorbers showed the presence of very soft electrons belonging to this activity; but since the 50-day activity was present in rather high intensity, the properties of the intermediate period could not be studied very well. But a similar mercury activity had been found[6] as a product of the deuteron bombardment of gold; and since gold has only one

[7] R. S. Krishnan, Proc. Camb. Phil. Soc. **37**, 186 (1941).
[8] R. Sherr, K. T. Bainbridge, and H. H. Anderson, Phys. Rev. **60**, 473 (1941).
[9] A. A. Noyes and W. C. Bray, *A System of Qualitative Analysis for the Rare Elements* (Macmillan Company, New York, 1927), pp. 113–116.

stable isotope, it was decided to bombard gold with 14-Mev deuterons and to study the mercury activities produced, and then to investigate whether they were identical with any of those found in neutron bombardments of mercury.

The half-life of the mercury fraction separated from the gold was again found to vary between about 30 and 45 hours, when different samples and different instruments were used. After the chemical identity had been definitely proved by repeated distillations, a thin sample was prepared by amalgamating a silver surface with the active mercury, and its decay was carefully followed on a Lauritsen electroscope. It was then found that the decay curve (when plotted on semilog paper) was not a straight line, but showed a slight curvature, the apparent half-life varying from 26 hours, a few hours after bombardment, to about 48 hours, after two weeks. This suggested immediately that there were two activities of rather similar half-lives. After following the decay of one sample for over a month on a Geiger-Mueller counter with a thin mica window, the decay curve could be resolved into two straight lines, corresponding to half-lives of 23 and 64 hours, respectively (Fig. 1). Aluminum absorption curves taken at various intervals

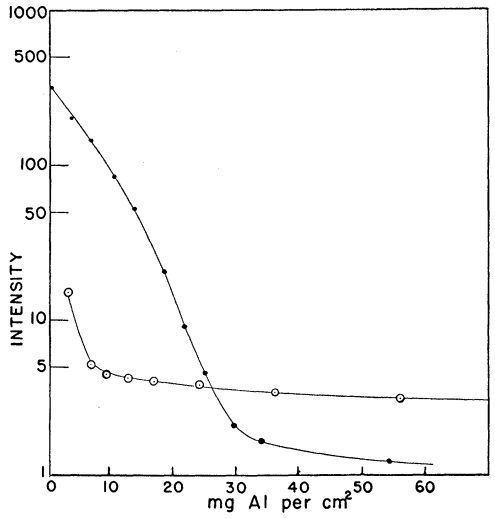

FIG. 2. Absorption in aluminum of the radiation from Hg^{197} produced by the bombardment of gold with 14-Mev deuterons. Dots indicate points taken two days after bombardment (mixture of 23-hour and 64-hour activities). Circles indicate points taken 15 days after bombardment (practically pure 64-hour activity). Two different aliquots were used for the two absorption curves.

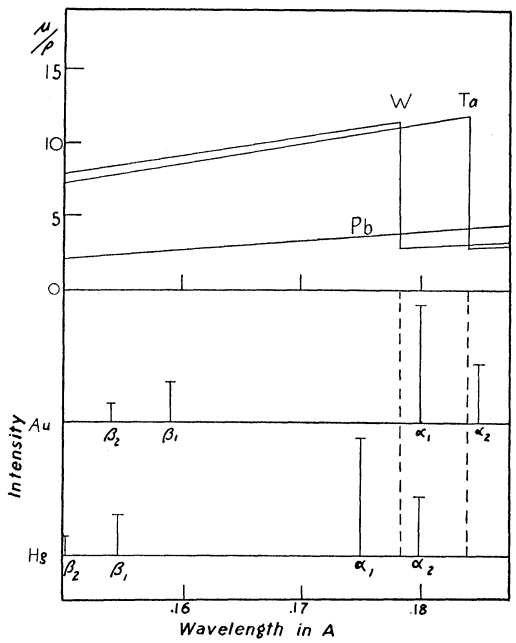

FIG. 3. The bottom part of the figure shows the K-emission lines of mercury and gold, with their relative intensities. The top part shows the mass absorption coefficients μ/ρ of tungsten, tantalum, and lead in the same wave-length region.

also showed clearly the presence of two different activities. Figure 2 shows absorption curves taken 2 days and 15 days, respectively, after bombardment. At the time the second curve was taken, the decay curve showed that the 23-hour period had practically completely disappeared. The end points of the absorption curves indicate maximum energies of about 200 and 90 kev respectively for the 23-hour and 64-hour activities. Dr. A. C. Helmholz[10] investigated the internal conversion electrons from some of our samples in his magnetic spectrograph and found K, L, and M lines from two gamma-rays decaying with a 25-hour half-life and L and M lines from a gamma-ray decaying with a 64-hour half-life. Valley[11] has also reported electron lines from mercury formed by deuteron bombardment of gold.

The only two mercury isotopes that can be formed in the deuteron bombardment of Au^{197} (if we assume the ordinary nuclear reactions) are Hg^{197} and Hg^{198}, the former by a d-$2n$, the latter by a d-n reaction. The fact that, in the

[10] A. C. Helmholz, Phys. Rev. **61**, 204 (1942).
[11] G. E. Valley, Phys. Rev. **60**, 167 (1941).

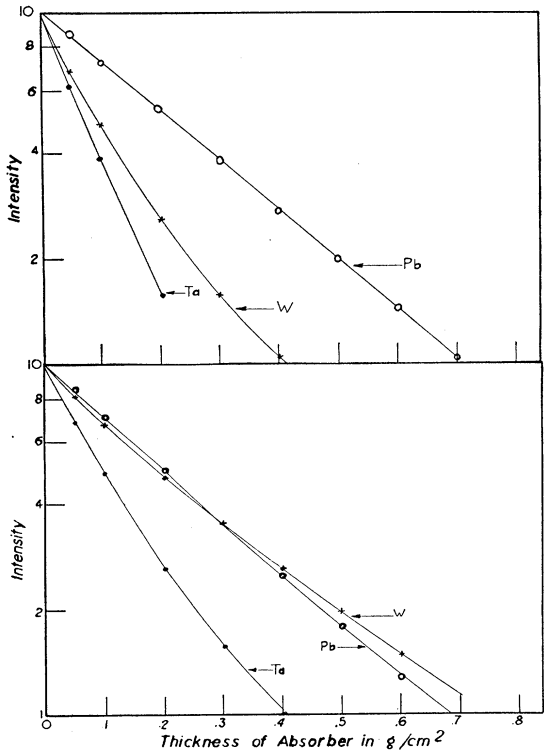

FIG. 4. Calculated curves for the absorption of the K radiations of mercury (upper curve) and gold (lower curve) in tungsten, tantalum, and lead.

bombardment of gold with 8-Mev deuterons from the 37-inch Berkeley cyclotron, we obtained an exceedingly small yield of mercury activity suggested that both periods were due to Hg^{197}, because at that bombardment energy the probability of a d-$2n$ reaction would be expected to be much lower than that of a d-n reaction. The possibility that one of the two activities was due to an excited state of Au^{197} or to Au^{198} growing out of active Hg^{197} or Hg^{198*} was eliminated: Chemical separations of gold and mercury were carried out by distillation at various intervals after bombardment, and in all cases the total activity stayed in the mercury fraction.

The final assignment of the two activities was made by means of critical absorption measurements of the x-rays emitted. The method was based on the following reasoning: Hg^{197} would be expected to decay by K-electron capture[12] to Au^{197}. The product of the disintegration would, therefore, be a gold atom with a vacancy in the K shell. Hence, outer electrons would be expected to cascade down to the K shell, with the emission of gold x-rays. An isomeric transition in mercury, on the other hand (e.g., from Hg^{198*} to Hg^{198}, or possibly from an upper to a lower level in Hg^{197}), would leave a mercury atom with a missing K electron as the reaction product; hence it would be followed by the emission of mercury x-rays. Thus, it could be hoped that an investigation of the x-rays emitted by the two mercury isotopes would throw some light on their modes of disintegration.

The four prominent K lines in the x-ray emission spectra of elements in the region of gold are (in the order of decreasing intensity): α_1, α_2, β_1, β_2. The wave-lengths and relative intensities of these lines are shown for mercury and gold in Fig. 3. On the same figure are shown the x-ray absorption spectra of tungsten, tantalum, and lead (the mass absorption coefficient

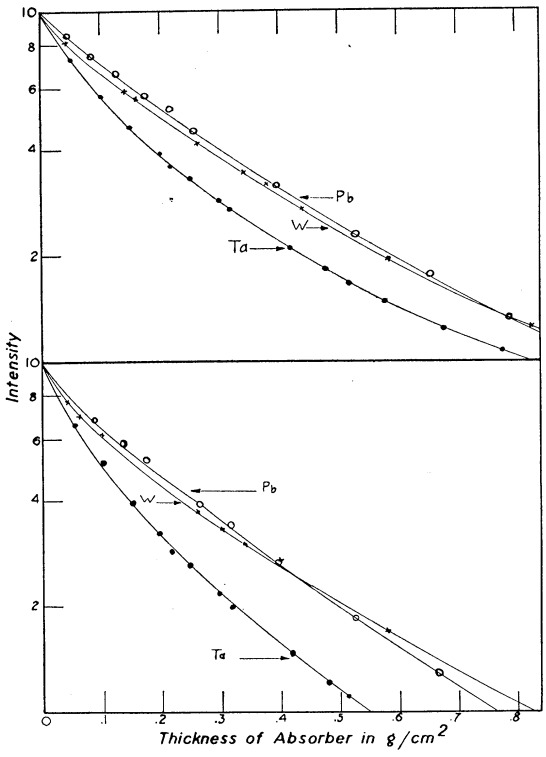

FIG. 5. Absorption in tungsten, tantalum, and lead of the x-rays emitted by Hg^{197}. The upper set of curves was taken 2 to 4 hours after the bombardment of gold with deuterons, the lower set of curves two weeks later.

[12] The alternative process of positron emission is very rare in the region of the heaviest elements. Furthermore, we were unable to detect experimentally any positrons in the mercury activities considered.

μ/ρ is plotted against wave-length). It is seen that the absorption edges of tungsten and tantalum fall in the region of the K-emission lines of gold and mercury. The data represented in Fig. 3 are taken from the book by Compton and Allison.[13] Absorption curves for the K x-rays of gold and mercury in tantalum, tungsten, and lead were calculated from these data and are shown in Fig. 4. If the original intensity of radiation is I_0, the intensity I which is transmitted through a thickness x of an absorber of density ρ is given by the formula $I=I_0e^{-\mu x}=I_0\cdot e^{-(\mu/\rho)\cdot(x\rho)}$. μ is the fractional reduction of intensity per cm of path length, and μ/ρ is called the mass absorption coefficient. Thus, if μ/ρ is known for a given wave-length (say, that of the $K\alpha_1$ radiation of gold) and a given absorber (say, tantalum), the intensity transmitted can be calculated as a function of the product of thickness and density ($x\rho$, expressed in g/cm^2). In this way the absorption curves in Fig. 4 were calculated. (They show the integrated effect of the 4 principal K-emission lines.)

Actual absorption curves of the x-rays emitted by the mercury fraction of the gold+deuteron bombardment were taken with tungsten, tantalum, and lead absorbers, at frequent intervals from the time of the chemical isolation of the mercury until two weeks later. The measurements were made with a freon-filled ionization chamber connected to a vacuum-tube electrometer with a sensitive galvanometer. In all the measurements an aluminum absorber of sufficient thickness to cut out all the electrons emitted was interposed between the sample and the window of the ionization chamber. This absorber also cut out the L radiations of gold and mercury, which are very much softer than the K radiations. Lead and tantalum foils were available in thicknesses from 0.001 inch up. But thin tungsten absorbers had to be made from tungstic oxide (WO_3). Suspensions of weighed amounts of WO_3 in an acetone solution of "Duco cement" were filtered quantitatively through sintered-glass funnels covered with filter paper. The dried precipitates were quite uniform and adhered well to the paper. The absorption of x-rays by the paper and by the oxygen in the WO_3 is negligible.

Two of the sets of experimental absorption curves are reproduced in Fig. 5. One was taken two hours after bombardment, the other one two weeks later. The two sets of curves are very similar (as are all the sets taken at various times) and both agree rather well with the calculated absorption curves for gold x-rays while they are very different from the calculated curves for mercury x-rays (Fig. 4). The deviations from the theoretically expected curves are due to the fact that both the 23-hour and the 64-hour periods have groups of soft gamma-rays associated with them. Although an attempt has been made to correct for the absorption of the gamma-rays, this could not be done quite satisfactorily, because of the complexity of the gamma-ray spectra and, in the later measurements, because of the weak activity of the samples.

The results of the x-ray absorption measurements leave no doubt that both the 23-hour and the 64-hour activities emit the K radiations of gold, and, therefore, that they decay by K-electron capture to form gold isotopes. The rather improbable case that one of them is an excited state of Hg^{198} and decays by K-electron capture to Au^{198} (which itself decays with a 2.7-day half-life to stable Hg^{198}) is completely ruled out by the fact that no growth of gold activity was observed. Thus, both periods can be assigned to Hg^{197}. Apparently the two isomeric states decay independently to Au^{197}, both by K-electron capture.

It should be pointed out here that Krishnan[6,7] has also used the critical absorption of x-rays to assign what he calls the 32-hour mercury activity, produced by deuteron bombardment of gold (probably a mixture of the 23-hour and 64-hour periods). His data agree with those of the present authors; but he merely compared the absorption curves of the x-rays from the "32-hour" mercury activity in tungsten, tantalum, and lead with those obtained with the x-rays emitted by the 43-minute mercury activity (cf. below). Finding the two sets of curves very different and having assigned the 43-minute period to Hg^{197} because it is produced by fast and not by slow neutrons in mercury, he concluded that the 43-minute activity emitted gold x-rays;

[13] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Company, New York, 1935).

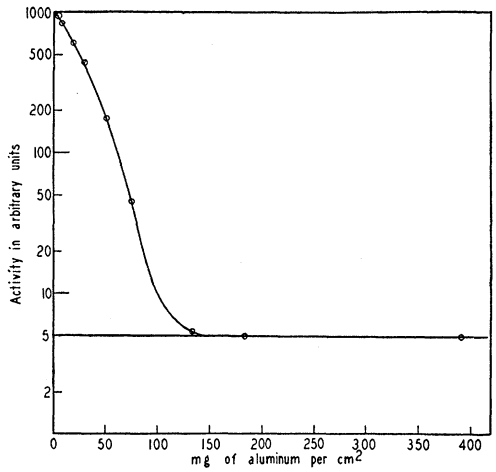

FIG. 6. Absorption in aluminum of the radiation from the 43-minute mercury activity.

the 32-hour activity mercury x-rays. He therefore assigned the latter to Hg^{198*}.

X-ray absorption curves were also taken on neutron-bombarded mercury samples, and the curves obtained after the 43-minute period had decayed completely agree very well with those taken on the mercury samples extracted from deuteron-bombarded gold. Thus it is probable that the complex activities at intermediate half-lives produced by neutron bombardment of mercury as mentioned at the beginning of this section are identical with the 23-hour and 64-hour periods produced from gold with deuterons. Apparently both slow and fast neutrons produce these periods in mercury, slow neutrons, however, in low intensity.

THE 43-MINUTE ACTIVITY

In fast neutron bombardments of mercury, a 43-minute mercury period is strongly induced. Slow neutron bombardments yield very little, if any, of this activity. The radiations associated with this period consist of conversion electrons, soft gamma-rays and x-rays.

Absorption measurements with aluminum absorbers (Fig. 6) suggest the presence of a line of electrons, rather than a beta-ray spectrum. The range of the electrons is about 140 mg/cm² of aluminum, corresponding to an energy of about 460 kev, according to the data of Varder and Eddy.[14]

[14] E. Rutherford, J. Chadwick, and C. D. Ellis, *Radiations from Radioactive Substances* (Cambridge University Press, 1930), p. 422.

The x-rays emitted by the 43-minute activity were investigated by the critical absorption method described in the preceding section. After the proper corrections were made for the rather intense gamma-rays of the 43-minute activity and for the presence of the 23-hour and 64-hour periods, the absorption curves in lead, tungsten, and tantalum agreed reasonably well with those calculated for the K radiation of mercury, as is seen from the set of experimental absorption curves reproduced in Fig. 7. Hence, the 43-minute period is associated with an isomeric transition in mercury.

To decide on the assignment of this activity, several additional experiments were performed. A careful search for the 43-minute period was made in the mercury fraction obtained from the bombardment of gold with 14-Mev deuterons. But no trace of this period was found. Hence it cannot be due to Hg^{197} or Hg^{198}. Very likely, it is an isomer of one of the stable isotopes of mercury (their mass numbers are: 196, 198, 199, 200, 201, 202, 204). The large yield of 43-minute activity from fast neutron bombardment of mercury makes the assignment to Hg^{196*} quite unreasonable, because Hg^{196} has an abundance of only 0.15 percent. If, on the other hand, the 43-minute period is associated with an isomeric state in one of the isotopes 199, 200, 201, or 202, the very low yield from slow neutron bombardment of mercury is difficult to explain, since any one of the isotopes named would be expected to be formed by an n-γ reaction from the next lower stable isotope. The best assignment, then, would seem to be Hg^{204*}, formed from stable Hg^{204} by excitation either with fast neutrons or with

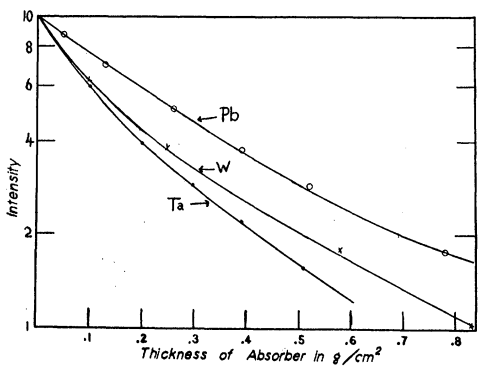

FIG. 7. Absorption in tungsten, tantalum, and lead of the x-rays emitted by the 43-minute mercury activity.

deuterons.[6] To test this assignment, it was thought advisable to bombard lead with fast neutrons, in the hope of forming Hg^{204*} from Pb^{207} by an n-α reaction. Spectroscopically pure lead was bombarded for several hours with the neutrons formed in the bombardment of beryllium with 14-Mev deuterons. The lead was amalgamated after bombardment and the mercury distilled off in vacuum. In each of two bombardments the mercury activity obtained was too small to be measured with any accuracy (0 ± 10 counts per minute on a Geiger-Mueller counter). It is to be remembered, however, that the neutrons used have an energy of about 18 Mev and that this may be below or near the threshold of the n-α reaction for an element as heavy as lead. The evidence against the assignment of the 43-minute period to Hg^{204*} may therefore not be conclusive.

Sherr, Bainbridge, and Anderson[8] have discussed the assignment of the 43-minute mercury activity. These authors produced that activity by fast neutron bombardment of mercury, and their results are in agreement with the ones discussed above. However, they have also obtained

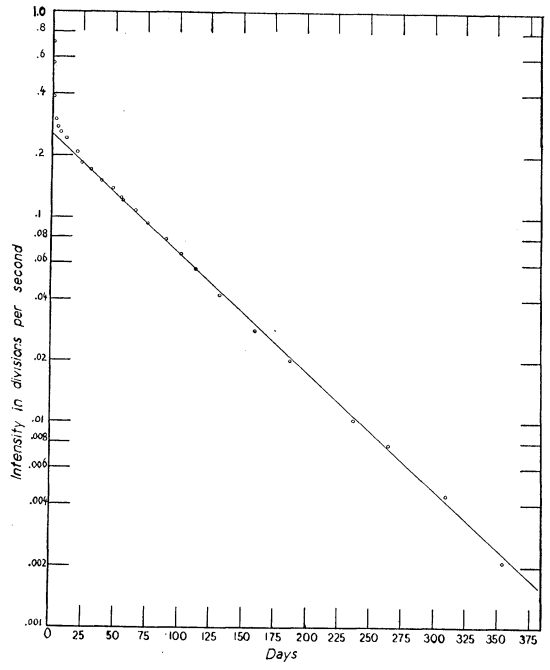

FIG. 8. Decay of the long-lived mercury activity produced by slow neutron bombardment of mercury. Half-life is 51.5 ± 1.5 days.

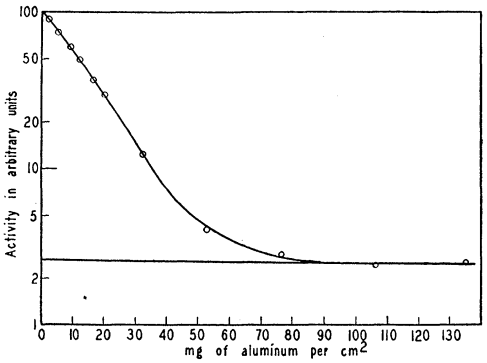

FIG. 9. Absorption in aluminum of the radiation from the 51.5-day mercury activity.

a 43-minute activity (chemically not identified) from the bombardment of platinum with alpha-particles. The properties of this activity are very similar to those of the 43-minute mercury. If the two are identical, then the assignment is limited to Hg^{199*} or Hg^{201*}, and the abnormally low yield with slow neutrons on mercury remains unexplained.

THE 51.5-DAY ACTIVITY

Krishnan and Nahum[6,7] mention that they have obtained a period of 60 days in their deuteron bombardments of mercury, but have not investigated this activity. Sherr, Bainbridge, and Anderson[8] observed a 50-day period in neutron bombardments of mercury, but did not study this activity. We have observed a period of similar half-life in the bombardment of mercury with slow or fast neutrons. Chemical separations proved this period to be associated with a mercury isotope. One sample was followed for one year (about seven half-lives) and found to decay with a half-life of 51.5 ± 1.5 days (Fig. 8).

This activity emits beta- and gamma-rays. The sign of the beta-rays was investigated by means of a magnetic field, in conjunction with a Geiger-Mueller counter. No positrons could be detected. A search for annihilation radiation also failed. The range of the beta-rays in aluminum (Fig. 9) is about 90 mg/cm^2, corresponding to a maximum energy of about 460 kev. The gamma-rays have a half-thickness of 1.25 g/cm^2 in lead corresponding[15] to an energy of 300 kev. No x-rays are emitted by this activity.

[15] W. Gentner, Physik. Zeits. **38**, 836 (1937).

The assignment of the 51.5-day activity is probably limited to Hg^{203} and Hg^{205}, since it decays by the emission of negative beta-particles to thallium. Tl^{203} and Tl^{205} are the only stable thallium isotopes, and no active thallium has been found to grow from the 51.5-day mercury. Since both slow and fast neutrons produce the activity, the best assignment is Hg^{203} which can be produced by n-γ reaction from Hg^{202}, and by n-$2n$ reaction from Hg^{204}.

THE 5-MINUTE ACTIVITY

In short slow neutron bombardments of mercury, an activity with a half-life of about 5 minutes was produced. No chemical identification of this activity was attempted. Its yield at saturation was about one-tenth of that of the 43-minute activity, which has itself an abnormally low yield in slow neutron bombardments. It cannot, therefore, be decided whether or not this period is due to an impurity. It may, however, be identical with the 5.5-minute mercury, reported by Krishnan and Nahum,[6] and assigned by them to Hg^{205}. We have not studied the radiations emitted by the 5-minute activity.

It is a pleasure to express our gratitude to Professor E. O. Lawrence for his interest and to the staff of the Radiation Laboratory for their cooperation. We are indebted to Professor G. T. Seaborg, Dr. J. W. Kennedy, and Dr. E. G. Segrè for numerous stimulating discussions and suggestions. The financial support of the Research Corporation and the Rockefeller Foundation is gratefully acknowledged.

PHYSICAL REVIEW VOLUME 63, NUMBERS 7 AND 8 APRIL 1 AND 15, 1943

Further Tests of the Atom-Annihilation Hypothesis as to the Origin of the Cosmic Rays

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(Received January 28, 1943)

1. Tests in Mexico. The authors had predicted that since the hypothetical silicon-annihilation rays should have enough energy (13.2 Bev) to get vertically through the earth's magnetic field at the equator in Peru, though not in India, there should be found, both at sea level and at all altitudes in the Americas, when vertically incoming rays alone are under test, a very long plateau of uniform cosmic-ray intensities extending north from Mollendo, Peru to about the latitude of Victoria, Mexico (mag. lat. 32.8°). There the strong band due to oxygen annihilation rays (7.5 Bev) should first appear, to be followed in going still further north when the latitude of 40° N magnetic had been reached, by the full entrance of the nitrogen annihilation band (6.5 Bev). The experimental findings were in accord with these predictions. 2. Tests in the United States. In going from Pasadena (mag. lat. 40.7° to St. George, Utah, but 4.1° (280 miles) nearer to the N magnetic pole than Pasadena, the carbon-annihilation band (5.6 Bev) was expected to appear, to be followed by a flat plateau clear up to latitude 54° N magnetic, when helium annihilation rays (1.88 Bev) were expected to appear. A balloon flight at St. George (mag. lat. 44.8°) and another at Pocatello, Idaho (mag. lat. 51°) yielded preliminary results in harmony with these predictions. 3. Evidence that the act of atom-annihilation actually transforms the rest mass energy of an atom into an electron pair. The flat plateau between St. George and Pocatello (mag. lat. 51°) corresponding to the absence of abundant atoms of atomic weight between that of carbon and that of helium, and the definite appearance of a new band between Omaha (mag. lat. 51.3°) and Bismarck (mag. lat. 56°) constitute new and strong evidence for the transformability of the complete rest mass energy of an atom into an electron pair.

I. THE FUNDAMENTALS OF THE HYPOTHESIS

IN a former paper[1] we have presented what may be called the atom-annihilation hypothesis of the origin of cosmic rays and the preliminary evidence found for its utility. This hypothesis assumes that an atom out in interstellar space has the capacity not possessed by an atom in the stars or in any other region in which it is continuously subjected to bombardment from neighboring atoms, of occasionally transforming the whole of its rest mass energy into a charged-particle pair which for the present

[1] Millikan, Neher, and Pickering, Phys. Rev. **61**, 397–413 (1942).