[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Neutron-deficient Mercury Isotopes[1]

BY RICHARD W. FINK AND EDWIN O. WIIG

RECEIVED AUGUST 13, 1951

High energy bombardments with protons on gold and α-particles on platinum were performed to study neutron-deficient mercury isotopes. Two new mercury isotopes have been definitely identified: Hg^{192}, $T_{1/2} = 5.7 \pm 0.5$ hours, 1.18 mev. β^+, 0.18 mev. conversion electrons, K, L X-rays and 1.39 mev. γ-ray; parent of 4.0 hour Au^{192}. Hg^{193}, $T_{1/2} = 10.0 \pm 0.5$ hours Noβ^+, K, L X-rays, 0.18 mev. conversion electrons; parent of 15.3 hour Au^{193}. Tentatively identified was Hg^{195} of 31 hour half-life, although this value may be in error owing to masking by the isomeric pair at Hg^{197}. Decay of Hg^{195} leaves gold daughter of 180-day half-life; although this genetic relation has not been established quantitatively, long-lived gold daughter has been observed. No positrons are emitted by Hg^{195} but K and L X-rays are detected. No activity was found which can be allocated to Hg^{194}. Positron-emitting 39.5-hour Au^{194} was not present among the gold daughters. An unidentified 2.0-hour mercury activity, present in increasing yield with increasing proton bombardment energy, must have mass number 191 or lower. Finally, the genetic relationships between Hg^{192}–Au^{192} and between Hg^{193}–Au^{193} have been established quantitatively.

Neutron-deficient isotopes of mercury have been studied by irradiation of platinum with 65 mev. α-particles for three hours in the Berkeley 184-inch cyclotron, as well as with 30 to 60 mev. protons on gold for periods of from one to three hours. Bombardments of gold with 55, 65 and 96 mev. protons were performed in the Rochester 130-inch cyclotron.

A 0.005-inch thick platinum target, irradiated with 65 mev. α-particles was dissolved in hot aqua regia, 10 mg. each of gold and mercury carriers added, and after evaporation to expel HNO_3 and dilution to 6 N HCl concentration, the solution was extracted with five successive portions of isoamyl acetate saturated with HCl just before use. The aqueous layer remaining was treated with excess $SnCl_2$ and the resulting precipitate of Hg_2Cl_2–Hg^0 washed free of red platinous ion color and until the washings exhibited little residual radioactivity. The precipitate was then dissolved in dilute aqua regia and utilized as the mercury fraction. From this bombardment the mercury half-lives observed were 5.5 hours, 9.6 hours, and longer-lived activity of the order of 24 to 40 hours and 64 hours half-life. The 24 to 40-hour portion is presumed to represent a mixture of Hg^{195} and the isomeric pair at Hg^{197} which is well studied.[2] No α-emission was observed from these mercury activities.

A Berkeley bombardment of 0.003-inch gold foil with 30 mev. protons for one hour gave a mercury activity of 31-hour half-life plus a long-lived activity of several months duration (presumably 180-day Au^{195} daughter) as shown in Fig. 1. The sample giving this long-lived tail was subjected to repurification experiments, using the chemical extraction procedure described above, which demonstrated that it was gold activity and not mercury. It is thus rather certain that the long-lived tail is 180-day Au^{195}, which is the only gold activity known to have a half-life of this order of magnitude reported in the literature.[3,4]

A Rochester bombardment with 50–55 mev. protons on 0.003-inch gold foil of 99.999% spectroscopic purity, obtained from Johnson–Matthey & Co. Ltd. (London), showed mercury half-lives of 10.0 hours, curve A of Fig. 2, and longer-lived components presumably composed of Hg^{195} and the 24-hour, 64-hour isomeric pair at Hg^{197}, as shown in curves B and C of Fig. 2. In this and all other gold bombardments, mercury was separated from the gold foil target by carrier-free volatilization. A portion of the gold target was placed in the chamber of a stainless steel vaporizer. A clean platinum collecting plate was cemented to a stainless steel cold-finger which was cooled with flowing cold water. The bottom of the apparatus was heated for about five minutes with a Fisher burner to not more than about 400°. Since the vapor pressure of pure mercury at 400° is 1574.1 mm., of pure molten gold at 1292° is only 0.001 mm., and of pure thallium at 413° is only 0.001 mm., this volatilization procedure affords a mercury separation which is quick, carrier-free, and excellent with respect to purity. The gross decay curves, Fig. 2, of vaporized mercury fractions were in all cases identical to gross decay curves obtained from the mercury fraction isolated chemically.

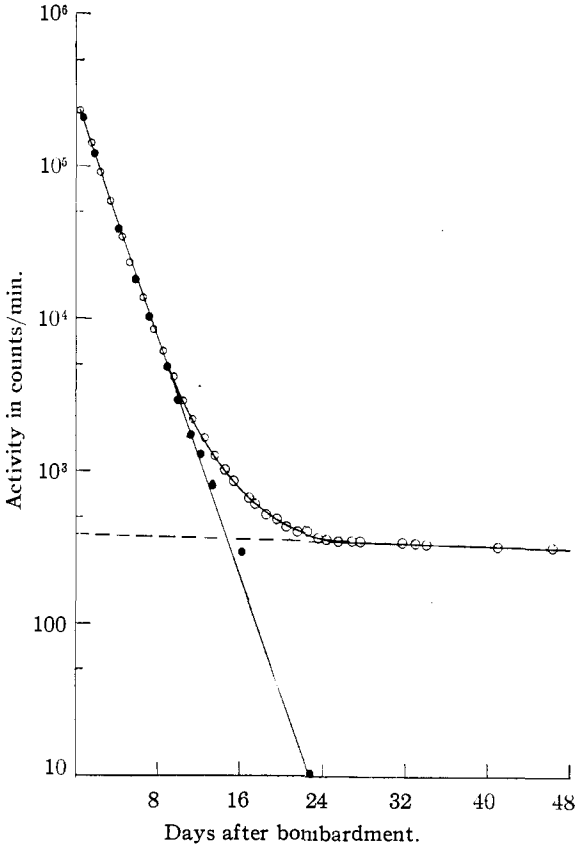

Fig. 1.—Gross decay of Hg fraction showing 31-hour Hg^{196} and long-lived (180-day) Au^{196} daughter resulting from bombardment of gold with 30 mev. protons.

As the energy of proton bombardment is increased to 65 mev. or greater, a new 5.7-hour mercury activity appears. The decay curve for a bombardment of gold foil with 96 mev. protons is shown in Fig. 3, where curve C represents the 5.7-hour mercury activity resulting from subtraction of longer-lived components from the gross decay curve. This 5.7-hour mercury activity was shown to yield a 4.0-hour

(1) This investigation was performed under contracts with the U. S. Atomic Commission, and was carried out partly at the Radiation Laboratory, University of California, Berkeley, and partly at the Department of Chemistry, University of Rochester, Rochester, New York.

(2) K. Way, L. Fano, M. R. Scott and K. Thew, National Bureau of Standards Circular 499, January 1, 1950.

(3) G. W. Wilkinson, *Phys. Rev.*, **75**, 1019 (1949).

(4) R. M. Steffen, O. Huber and F. Humbel, *Helv. Phys. Acta*, **22**, 167 (1949).

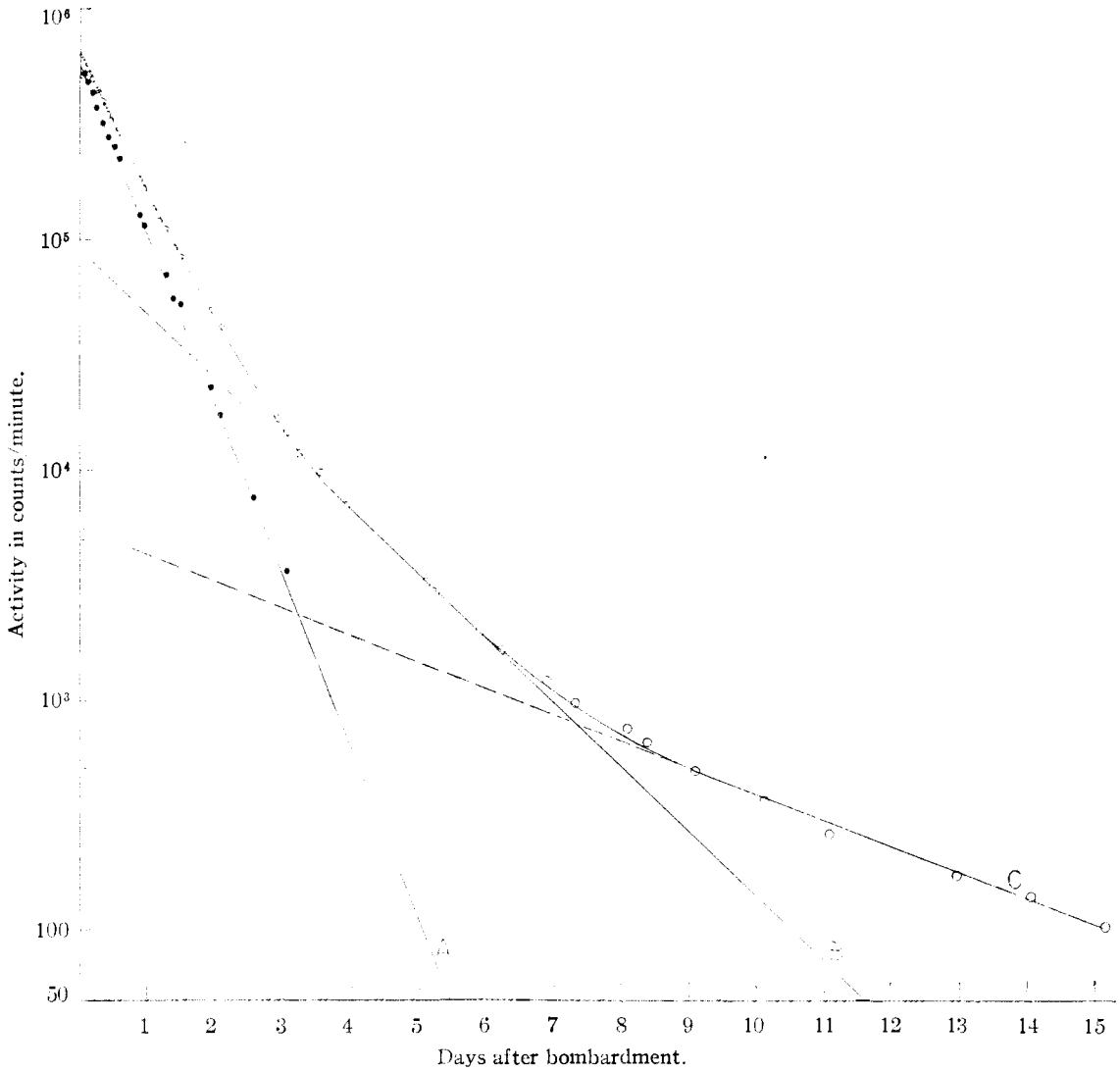

Fig. 2.—Gross decay of Hg fraction showing 10.0-hour Hg^{193}, curve A; and longer components of the order of 24 to 40 hours, curve B (representing a mixture of 31-hour Hg^{195} and 24-hour Hg^{197}); and 64-hour Hg^{197}, curve C, resulting from bombardment of gold with 50–55 mev. protons. Note absence of 5.7-hour Hg^{192} at this energy.

gold daughter. These do not appear at bombardment energies lower than about 60 mev. Through identification of 4.0-hour Au^{192} daughter, the 5.7-hour mercury is shown to have mass number 192. With 96 mev. protons a greatly increased yield of 5.7-hour activity relative to 10.0-hour mercury is observed and a new 2.0-hour activity, Fig. 3 curve B, appears in high yield. The assignments and genetic relationships are given below.

Mercury 195.—A 31-hour activity from 30 mev. proton bombardment of gold is assigned to Hg^{195}, although this half-life may be in error by as much as 20% owing to masking by the 24-hour, 64-hour isomeric pair at Hg^{197}. A long-lived gold daughter is observed which is presumed to be Au^{195}. This genetic relationship has not been proved quantitatively. No positrons are observed with a 4.0 cm. magnetic spectrometer, but L X-rays of 10.5 kev. energy and conversion electrons of 0.19 mev. are observed in aluminum–beryllium absorption measurements.

Mercury 194.—Although the interesting nucleus Hg^{194} was undoubtedly produced in these bombardments, no activities were observed which can be allocated to it, nor was its 39.5-hour, positron-emitting Au^{194} daughter ever observed from it. These findings are consistent with the hypothesis that Hg^{194} is probably stable.[5]

(5) C. W. Wilkinson, "Beta-particle, Orbital-Electron Capture Branching and Missing Beta-Stable Isotopes," UCRL-289 (1948).

Mercury 193.—A 10.0 ± 0.5 hour mercury activity which is produced with 55 mev., but not with 30 mev., protons and which diminishes in yield as the bombardment energy increases to 96 mev., is assigned to Hg^{193}. The requisite quantitative relationship between 10-hour mercury and 15.3 hour Au^{193} daughter[2,3] has been demonstrated. Parent–daughter separations were performed by extracting the 6 *N* HCl aqueous mercury fraction to which 6 mg. of gold carrier was added with isoamyl, or in some experiments with *n*-amyl, acetate saturated with HCl just prior to use, and then stripping the organic layer with 1 *N* NH_4Cl to remove any traces of mercury isotopes from the gold daughter fraction. The validity of this separation was studied with carriers and found to be of excellent quality. Light from a carbon arc was found not to reduce $HAuCl_4$ photochemically in the presence of mercury, so that extraction affords a clean mercury–gold separation. Isoamyl acetate is superior to ethyl acetate in micro-extractions because the latter is excessively soluble in water. Use of a small rheostated stirring motor fitted with flexible micro-stirring rods fashioned from thermoplastic Kel-F (poly-trifluorochloroethylene) quarter-inch rod greatly facilitates micro-extractions on quantities as small as 0.030 ml. In Fig. 4, curve B shows the decrease in yield of 15.3-hour Au^{193}, extrapolated to instant of isolation from the mercury parent, the slope being 10.6 ± 0.5 hours, in agreement with the 10.0 ± 0.5-hour half-life found for the parent, Hg^{193}. The successive separations of gold

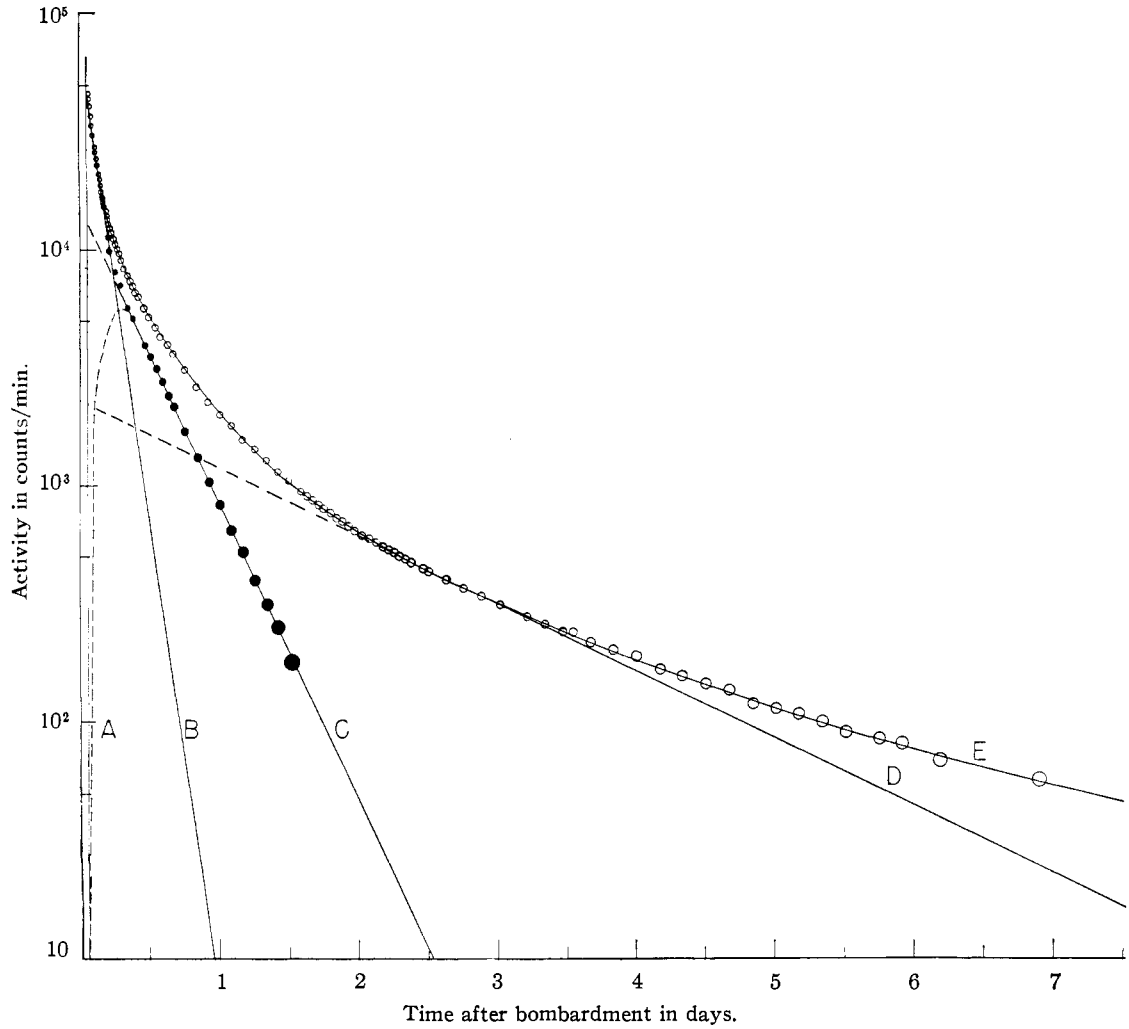

Fig. 3.—Resolution of gross decay curve of vaporized mercury fraction resulting from irradiation of gold with 96 mev. protons. Points at high counting rates were derived from data taken at lower geometry. Curve A shows the growth of 4.0-hour Au^{192} daughter calculated on the basis of equal detection efficiencies for parent and daughter. Curve B shows the unidentified 2.0-hour activity, possibly Tl^{198} or Hg^{191}. Curve C represents a half-life of 5.7 ± 0.5 hours, assigned to Hg^{192}. Curves D and E represent the presence of 24-hour, 64-hour Hg^{197} isomers. Curve E has been followed for 50 days in all; ultimately, it tails out to a very long-lived activity which was shown to be an isotope of gold (Au^{195}).

daughter from the mercury fraction were made at approximately equal time intervals so that the slope of the curve represents the half-life of the parent activity. Hg^{193} emits no observable positrons, but manifests 9.6-hour K and L X-rays as followed on an X-ray counter, fitted with a permanent alnico magnet of 1600 gauss and xenon-filled Geiger tube of such geometry that all particles of energy less than 2.4 mev. would be bent away and not counted. In addition, the sample was covered with 195 mg./cm.^{2} of beryllium and surrounded with lead housing. A 4.0-cm. magnetic spectrometer confirmed the presence of 0.18 mev. conversion electrons in agreement with aluminum–beryllium absorption curves. Gross decay of a typical gold daughter from this 50–55 mev. proton bombardment gave a half-life of 15.3 ± 0.5 hours for Au^{193}.

Mercury 192.—With protons of 60 to 96 mev. on 0.003-inch gold foil in the Rochester cyclotron, a new mercury activity of half-life 5.7 ± 0.5 hours is observed, as shown in Fig. 3, curve C, resolved in the usual manner. If curve C is extrapolated to the time of separation of mercury by volatilization from the gold target, then from the initial activity of Hg^{192} the growth of 4.0-hour Au^{192} daughter is calculated to follow curve A, assuming equal detection efficiencies. The latter joins curve C at about the time of maximum activity of parent and daughter (about 6.5 hours after separation) as it should on the assumption of half-lives of 4.0 and 5.7 hours for daughter and parent, respectively. The parent–daughter genetic relationship is shown quantitatively in Fig. 4, curve A, where the decrease in yield of Au^{192}, extrapolated back to instant of isolation from the mercury parent, approaches 5.6-hour half-life, in excellent agreement with the 5.7-hour half-life of the parent. The times of successive separation of daughter were approximately equal in duration and were far enough apart so that transient equilibrium of Hg^{192} growing into Au^{192} was attained between separations. Curves D and E in Fig. 3 represent the longer-lived activities due to the 24-hour, 64-hour isomeric pair at Hg^{197}, present in all bombardments.

Hg^{192} emits positrons of 1.18 mev. maximum energy detected on a 4.0-cm. magnetic spectrometer. Decay of the positron peak gave a half-life of roughly 6 hours. The maximum positron energy measured by aluminum–beryllium absorption curves agrees well with the magnetic spectrometer result. Thus, Hg^{192} is the highest atomic-numbered nuclide to emit positrons known to date. Lead absorption curves showed a 1.39 mev. γ-ray in addition to 0.5 mev. annihilation radiation associated with Hg^{192}. The decay curve of the gold daughter fraction isolated from the mercury fraction by isoamyl acetate extraction and followed by a scintillation counter fitted with a NaI(Tl) crystal and RCA 5819 photomultiplier tube gave a half-life of 4.13 ± 0.10 hours for Au^{192}.

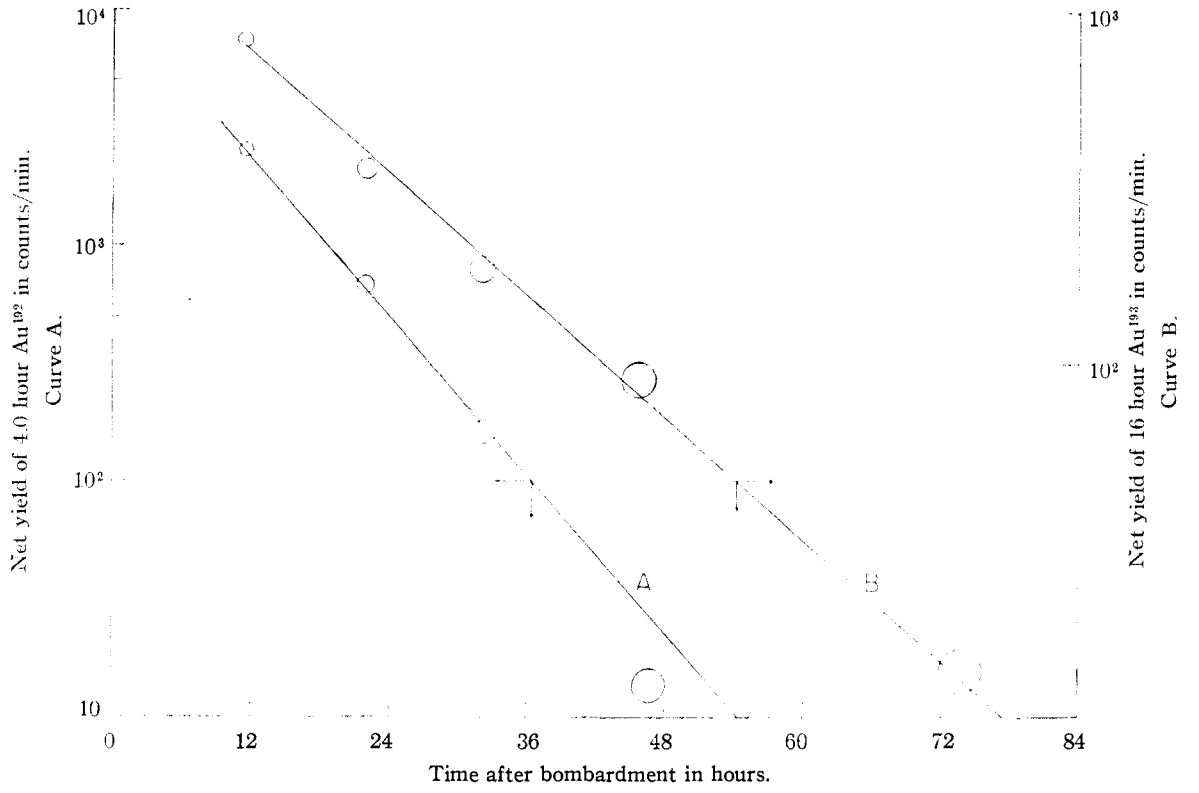

Fig. 4.—Net yield curves from bombardment of gold with 65 mev. protons. Curve A represents the yield of 4.0-hour Au^{192} daughter, extrapolated back to instant of isolation, while curve B represents the yield of 15.3-hour Au^{193} daughter, extrapolated back to instant of isolation. Since the time intervals between successive separations are longer than the time required for transient equilibrium in curve A, the slope of curve A, 5.6 hours, represents the half-life of Hg^{192} parent. Since the time interval between successive separations is approximately constant for the first four points of curve B, the slope represents the half-life of the parent, 10.6 hours, decaying into 15.3-hour Au^{193}. Note that curves A and B have different ordinates.

Other Activities Observed.—In the vaporized mercury fraction from 96 mev. proton bombardment of gold, an unidentified 2.0-hour activity occurs in high yield, shown in curve B of Fig. 3. This yield increases relative to other activities present as the energy of bombardment increases from 65 to 96 mev., indicating that this activity might belong to a mercury isotope of mass number 191 or lower. It also might possibly be Tl^{198} produced by a secondary $Au^{197}(\alpha,3n)$ reaction, though the high yield would seem to make this unlikely. The gold fraction from 60 mev. proton bombardments showed the presence of 13.8-hour Au^{196m} and 5.3-day Au^{196} as expected from a (p,pn) reaction. The platinum fraction showed a 4.3-day activity, Pt^{193}, and a 7.0-hour activity which is so far unidentified, but which might be Tl^{199} on the basis of the chemical scheme used.

Moon and Thompson[6] recently have reported results as follows: Hg^{195}, 38 hours; Hg^{194}, not found; Hg^{193}, 14.5 hours and 29.0 hours; Hg^{192}, 8.4 hours; and Hg^{191}, 12.4 hours; all are reported to be K-capturing isotopes. We believe the 8.4-hour period reported for Hg^{192} may be a mixture of 5.7-hour Hg^{192} and 10.0-hour Hg^{193}, and that the 14.5-hour and 29.0-hour periods reported for Hg^{193} are in error possibly due to masking by Hg^{197}, to presence of incompletely separated gold activities, or other error. The 38-hour value reported for Hg^{195} differs from our 31-hour value, but owing to masking by Hg^{197} this is not outside our experimental error. The 12.4-hour activity reported for Hg^{191} leading to an 18-hour gold daughter is felt to be in reality mass number 193, the half-lives appearing longer due to presence of Hg^{195} and Hg^{197} in the mercury sample and presence of Au^{196} and longer-lived gold in the gold daughter fraction. The chemical procedures used are not given in the brief report cited.

A preliminary report[7] of our results was published in the Revised General Electric Chart of the Nuclides.

Acknowledgments.—We are indebted to Dr. David H. Templeton of the Radiation Laboratory, University of California, Berkeley, for valuable suggestions and criticisms; to James T. Vale and the crew of the Berkeley 184-inch cyclotron; to Mr. James Norton of the Rochester 130-inch cyclotron for his assistance in design of cyclotron probes; and to Dr. Sidney W. Barnes and the crew of the Rochester cyclotron for assistance in bombardments.

ROCHESTER, NEW YORK

(6) J. H. Moon and A. L. Thompson, *Bull. Am. Phys. Soc.*, **26**, #5, 12 (1951).

(7) R. W. Fink, Private Communication to Dr. J. R. Stehn, Knolls Atomic Power Laboratory, Schenectady, New York, 1949.