Radioactive Isotopes of Zinc

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The existence of zinc radioactivities with half-lives 57 minutes and 13.8 hours is confirmed, by deuteron activation of zinc. In addition, it is found that both these activities are produced by deuteron and by fast neutron irradiation of gallium, so that the two periods must be due to isomers of Zn^{69}. Both emit negative electrons and the properties of their radiations are given. It is shown that Zn^{65}, produced through deuteron bombardment of zinc, has a half-life of 250 days, agreeing with the period found by others after proton and deuteron bombardment of copper. This isotope appears to decay by K electron capture and also, to a lesser extent, by positron emission. No evidence has been found for radioactive Zn^{71}. All previously reported zinc activities are discussed and the following table contains all the known periods that are believed to be genuine.

REACTION	HALF-LIFE	PARTICLE RANGE GRAMS/CM² Al	GAMMA-RAY HALF-THICKNESS GRAMS/CM² Pb
$Zn^{64}(\gamma, n)Zn^{63}$ $Zn^{64}(n, 2n)Zn^{63}$ $Cu^{63}(p, n)Zn^{63}$ $Ni^{60}(\alpha, n)Zn^{63}$	38±2 min. (+)	?	?
$Zn^{68}(d, p)Zn^{69}$ $Zn^{68}(n, \gamma)Zn^{69}$ $Ga^{71}(d, \alpha)Zn^{69}$ $Ga^{69}(n, p)Zn^{69}$	57±2 min. (−) and 13.8±0.4 hr. (−)	~0.4 0.40	None 3.7
$Zn^{64}(d, p)Zn^{65}$ $Cu^{65}(d, 2n)Zn^{65}$ $Cu^{65}(p, n)Zn^{65}$	250±5 days (+, and K electron capture)	0.20	9.6

THE study of the radioactive isotopes of zinc has been replete with confusion and contradiction. There is but one point upon which all observers have agreed: that Zn^{63} is positron-active with a half-life of 37 to 40 minutes. This activity has been produced by 17-Mev gamma-rays[1] on zinc through $Zn^{64}(\gamma, n)Zn^{63}$; by fast neutrons[2–5] on zinc through $Zn^{64}(n, 2n)Zn^{63}$; by helium ions on nickel[6] through $Ni^{60}(\alpha, n)Zn^{63}$, and by proton bombardment of copper[7, 7a, 8, 8a] through $Cu^{63}(p, n)Zn^{63}$. These experiments in themselves limit the choice of the isotope responsible to either Zn^{63} or Zn^{65}, but since slow neutron or deuteron bombardment of zinc has never produced the activity, one can be certain that it belongs to Zn^{63}.

Early work on the bombardment of zinc with neutrons was confused because of the production of an active nickel as well as an active zinc, in addition to two easily recognized copper periods. The half-life and chemical identity of this nickel (2.6 hours, Ni^{63} or Ni^{65}) has now been established,[9] so that it is possible to interpret reasonably the pseudo-periods that were obtained without benefit of a chemical separation of zinc from nickel. (The report by Rotblat[10] of a chemically identified nickel with 60 minutes half-life, produced by fast neutrons on zinc, has

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[1] W. Bothe and W. Gentner, Naturwiss. **25**, 191 (1937).
[2] M. L. Pool, J. M. Cork and R. L. Thornton, Phys. Rev. **52**, 239 (1937).
[3] F. A. Heyn, Physica **IV**, 1224 (1937).
[4] R. Sagane, Phys. Rev. **53**, 212(A) (1938), **55**, 31 (1938).
[5] R. L. Thornton, Phys. Rev. **53**, 326 (1938).
[6] L. N. Ridenour and W. J. Henderson, Phys. Rev. **52**, 139 (1937).
[7] L. N. Ridenour, L. A. Delsasso, M. G. White and R. Sherr, Phys. Rev. **53**, 770 (1938).
[7a] L. A. Delsasso, L. N. Ridenour, R. Sherr, M. G. White, Phys. Rev. **55**, 113 (1939).
[8] C. V. Strain and J. H. Buck, Phys. Rev. **53**, 943(A) (1938).
[8a] C. V. Strain, Phys. Rev. **54**, 1021 (1938).
[9] See J. J. Livingood and G. T. Seaborg, Phys. Rev. **53**, 765 (1938) for bibliography and discussion.
[10] J. Rotblat, Nature **139**, 1110 (1937).

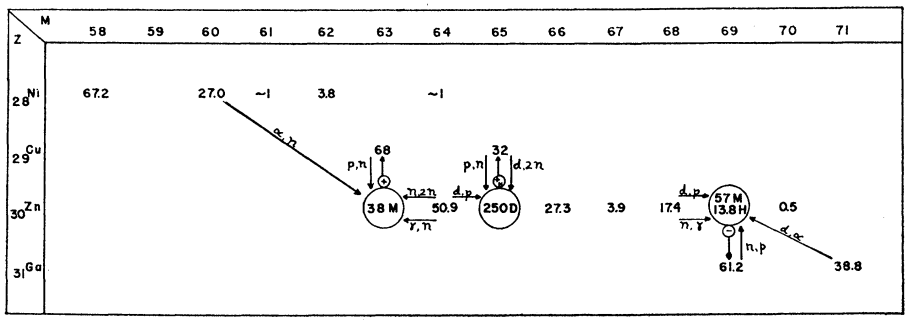

FIG. 1. Percent abundance of the stable isotopes in the neighborhood of zinc. The half-lives of radioactive forms of zinc are shown in circles; arrows indicate known transmutations.

not been confirmed and in our opinion must be considered to be in error.)

There is now some unanimity on the existence of a zinc isotope with half-life about one hour. This has been reported as produced by slow neutron[3, 4, 5, 11] and deuteron[5] bombardment of zinc and by deuteron activation of copper[5] (we will show that this last transmutation is probably erroneous). The emitted particles have been observed to be negative electrons by Sagane[4] and by Heyn.[11] The thickness of aluminum to reduce them to half-value is given by these authors as 0.06 and 0.04 gram per cm², respectively. This activity has been ascribed at various times both to Zn^{69} and Zn^{65}; the alternative choice of Zn^{71} is very improbable because of the low abundance of stable Zn^{70} (0.4 percent).

A weak zinc activity of 10 hours half-life has been found by Thornton[5] after slow neutron activation of zinc; this is probably the same as a stronger 14-hour zinc period obtained by him following bombardment of zinc with fast neutrons and also after deuteron bombardment of zinc and of gallium. This activity has been assigned to Zn^{69}, since the $Ga(d, \alpha)Zn$ reaction could lead but to this one beta-particle emitting zinc isotope.

Thornton has also reported[5] a weak 4-day zinc period after activating zinc with deuterons. This has been shown by Alvarez[12] actually to be Ga^{67}, formed by $Zn^{66}(d, n)Ga^{67}$; the same gallium period has been obtained by Mann[13] through $Zn^{64}(\alpha, p)Ga^{67}$ and by Strain and Buck[8] through $Zn^{67}(p, n)Ga^{67}$ or $Zn^{66}(p, \gamma)Ga^{67}$. We also have confirmed this identification, after deuteron activation of zinc (unpublished).

Thornton also states[5] that a weak zinc activity with 30 days half-life is produced by deuteron bombardment of zinc and suggests that it be due to Zn^{71}.

Perrier, Santangelo and Segrè[14] have reported a zinc activity with 245 days half-life from deuteron activated copper. Barnes and Valley[15] quote a 7-month period from proton activated copper. We have reported[16] a 7-month zinc period from zinc bombarded with deuterons. In our opinion, for which we will give evidence further on, Thornton's 30-day figure is to be interpreted as an indication of this longer period and not as a separate activity.

In this paper we propose to show conclusively that the 7-month activity is due to Zn^{65} and that the one-hour and 14-hour periods are isomers of Zn^{69}. To aid in understanding the arguments, the known stable isotopes[17] in the pertinent region are displayed in Fig. 1, with the radioactive forms of zinc shown in circles. The bombardments were made with the Berkeley cyclotron, with deuteron currents up to 100 microamperes at eight Mev. The activities were observed with an air-filled quartz-fiber electroscope with a thin window of 0.0001 inch aluminum. For deuteron bombardments, C.P. sticks or sheets of zinc were soldered to a water-cooling pipe and activated in vacuum; the surface was

[11] F. A. Heyn, Nature **138**, 723 (1936).
[12] L. W. Alvarez, Phys. Rev. **53**, 606 (1938).
[13] W. B. Mann, Phys. Rev. **54**, 649 (1938).
[14] C. Perrier, M. Santangelo and E. Segrè, Phys. Rev. **53**, 104 (1938).
[15] S. W. Barnes and G. Valley, Phys. Rev. **53**, 946(A) (1938).
[16] J. J. Livingood and G. T. Seaborg, Phys. Rev. **54**, 239 (1938).
[17] M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. **9**, 380 (1937).

then filed to obtain the radioactive metal. For gallium, the deuterons were passed through a thin aluminum window into the air where they struck a puddle of molten gallium (melting point 30.1°C) supported in a depression in a carbon block. To obtain high intensities of fast neutrons, metallic lithium was pressed into a corrugated and water-cooled copper plate which was bombarded in helium at reduced pressure, the deuterons entering this subsidiary target chamber[18] through a thin aluminum foil.

All of the measurements were made upon chemically separated samples. The zinc was separated last, after the removal of other radioactive elements produced by the bombardments. The zinc from the Zn+D activations was dissolved in a mixture of dilute HCl and HNO_3 and small amounts of $GaCl_3$ and $CuCl_2$ were added to serve as carriers for the transmutation products copper and gallium. The solution was then adjusted to 6.0 *N* in HCl and the $GaCl_3$ was extracted with ether, according to the method of Noyes and Bray.[19] Complete removal of the $GaCl_3$ was insured by several additional shakings with fresh portions of ether. The HCl solution was then adjusted to a concentration one *N* and the copper was precipitated as CuS by introducing H_2S. After removal of the CuS by filtration, the filtrate was made alkaline with NH_4OH and the zinc was precipitated as ZnS upon the further addition of H_2S.

Essentially the same procedure was followed to separate zinc after the bombardments of gallium with neutrons. After deuteron bombardment of gallium, the gallium was dissolved in a mixture of HCl and HNO_3 following the addition of carrier $GeCl_4$ and $ZnCl_2$. The volatile $GeCl_4$ was distilled off and the $GaCl_3$ was extracted with ether in the manner described above. The zinc was then removed by precipitation as ZnS with H_2S from an alkaline solution.

Radioactive Isotope Zn^{69}: From Zn+D, Zn+n, Ga+D and Ga+n: Half-Lives 57±2 Minutes (−) and 13.8±0.4 Hours (−)

Figure 2 shows the decay of radioactive zinc separated from a bombardment of zinc for a few minutes with several microamperes of eight-Mev deuterons. The half-lives are 57 minutes and 13.8 hours; both activities emit negative electrons, as found by magnetic deflection. They must therefore be assigned to either Zn^{69} or Zn^{71} or to both. The initial activities, extrapolated back to the end of the bombardment, are 30 and 1.1 divisions per second, respectively; when corrected to infinite bombardment time these figures become 494 and 263 divisions per second, so that their ratio is 1.88. This number at once suggests the isomerism of the two periods, since the abundances of the stable isotopes Zn^{68} and Zn^{70} (17.8 percent and 0.4 percent) would lead one to expect a ratio of 44.5 if the activities were associated one with Zn^{69} and one with Zn^{71}.

In accord with the results of Thornton, we find that eight-Mev deuterons on gallium yield the 13.8-hour activity in the zinc precipitate. In addition, we find also the 57-minute period in the zinc. (See Fig. 2.) Both these activities have again been found to be electron emitters. This proves conclusively that the two periods are associated with one isotope and that this must be Zn^{69} since no other beta-particle emitting

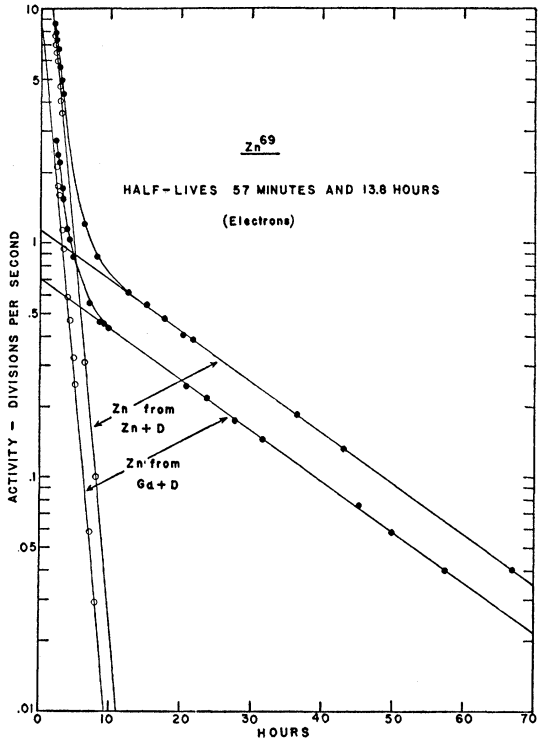

FIG. 2. Decay curves of Zn^{69}.

[18] F. N. D. Kurie, J. App. Phys. **9**, 691 (1938).
[19] A. A. Noyes and W. C. Bray, *Qualitative Analysis for the Rare Elements* (Macmillan Company, 1927).

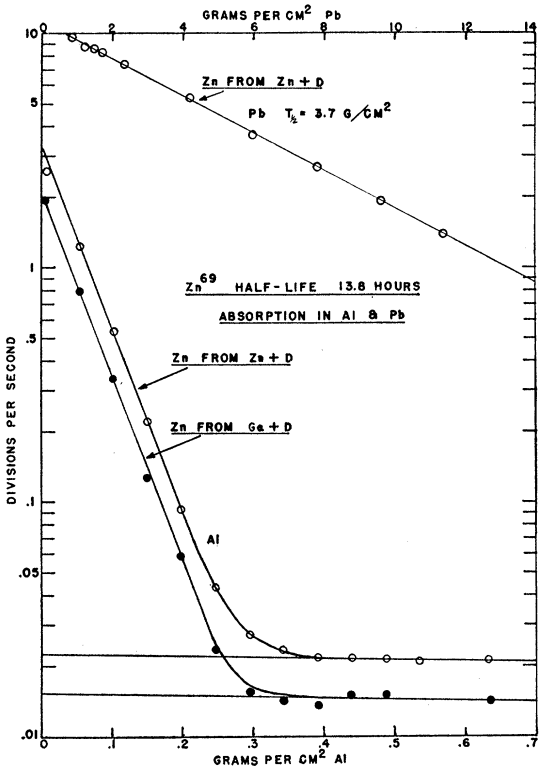

FIG. 3. Absorption curves of 13.8-hour period of Zn^{69}.

isotope can be formed. The initial intensities of the two activities when produced in this manner give a ratio of 2.00 after correction to infinite bombardment time. It is interesting to note that this value is practically the same as that found when the periods are produced by deuteron bombardment of zinc, as described above.

It is a disturbing coincidence that the period of Ga^{72}, known[4, 20] to be 14 hours, is almost identical with the 13.8-hour half-life of Zn^{69}. The doubt might arise as to whether the 13.8-hour activity observed in the zinc precipitate after deuteron bombardment of gallium is genuinely due to zinc or whether it is caused by incomplete removal of Ga^{72}; if the latter were true, this argument for the isomerism of the one-hour and 13.8-hour zinc periods would become invalid. To test this point, absorption data were taken on the 13.8-hour zinc from Ga+D. The resulting curve is practically indistinguishable from that of the 13.8-hour zinc from Zn+D, as is shown in Fig. 3; furthermore, the range and half-thickness of the electrons from the 14-hour Ga^{72} are unquestionably different, as we will show in a subsequent paper.

As a final check, we have bombarded gallium with the fast neutrons from Li+D and again have found in the zinc precipitate the 57-minute and 13.8-hour periods, both negative electron emitters. (The neutrons released during the deuteron bombardment of gallium may have enough energy to cause the Ga(n, p)Zn reaction, so that part of the intensity of the 57-minute and 13.8-hour periods observed after a Ga+D activation may be due to this mechanism; however, intensity arguments show that practically all the activities in this case must be due to the Ga(d, α)Zn reaction.)

We therefore feel that it has been demonstrated positively that both the 57-minute and 13.8-hour activities belong to Zn^{69}, and the modes of production are:

$$
\begin{aligned}
&{}_{30}Zn^{68}+{}_{1}D^{2}\rightarrow{}_{30}Zn^{69}+{}_{1}H^{1},\\
&{}_{30}Zn^{68}+{}_{0}n^{1}\rightarrow{}_{30}Zn^{69}+\gamma,\\
&{}_{31}Ga^{71}+{}_{1}D^{2}\rightarrow{}_{30}Zn^{69}+{}_{2}He^{4},\\
&{}_{31}Ga^{69}+{}_{0}n^{1}\rightarrow{}_{30}Zn^{69}+{}_{1}H^{1},
\end{aligned}
$$

which are followed in each case by

$$
{}_{30}Zn^{69}\rightarrow{}_{31}Ga^{69}+{}_{-1}e^{0}\quad 57\text{ min. and }13.8\text{ hr.}
$$

The only published report inconsistent with the above interpretation is that of Thornton, who reports[5] a 65-minute zinc isotope produced by bombarding copper with deuterons; this activity would have to be placed with Zn^{65} or Zn^{63} through Cu^{65}(d, $2n$)Zn^{65}, Cu^{63}(d, γ)Zn^{65} or Cu^{63}(d, $2n$)Zn^{63}. We have repeated this bombardment but have not been able to confirm Thornton's findings; any one-hour activity in the zinc precipitate was certainly less than one part in 10,000 of that of the 12.8-hour Cu^{64} period in the copper precipitate. If Thornton's yield of one-hour zinc was of this order of magnitude perhaps it could be accounted for by an impurity of stable zinc in the copper used by him.

An early report by one of us[21] that the bombardment of zinc with 3.2-Mev deuterons gives activities with half-lives one hour, 12 hours, 25 hours and 97 hours (without chemical

[20] J. J. Livingood and G. T. Seaborg, Phys. Rev. **54**, 51 (1938).

[21] J. J. Livingood, Phys. Rev. **50**, 425 (1936).

analysis) can now be interpreted reasonably as due to the formation of the 57-minute Zn^{69}, 66-minute Ga^{68}, 13.8-hour Zn^{69} (and possibly 12.8-hour Cu^{64}) and the 4-day Ga^{67} activities; the 25-hour period was probably a spurious apparent component of the complex decay curve.

Absorption data for the 13.8-hour activity from Zn+D and Ga+D are shown in Fig. 3. The electrons have a range of 0.40 ± 0.03 gram per cm^2 Al, corresponding to an energy of 1.1 Mev through the relation of Widdowson and Champion:[22]

$$E(\text{Mev}) = [\text{Range}(\text{grams}/\text{cm}^2) + 0.165]/0.536.$$

The gamma-ray is absorbed to half-value by 3.7 grams per cm^2 Pb, which indicates an energy of 0.4 Mev through the correlation of Gentner.[23]

Absorption data for the 57-minute activity, both from Zn+D and Ga+D bombardments, are shown in Fig. 4. These curves are the result of differences of data taken when both the 57-minute and 13.8-hour periods were present and when only the latter was left. Correction for decay was applied. It may be seen that no gamma-ray is present in the 57-minute activity. The electrons show a half-thickness of 0.033 gram per cm^2 Al and an estimated range of about 0.35 gram per cm^2, corresponding to an energy of roughly one Mev.

There is no evidence that there exists a genetic relationship between the two activities of this isomer of the type recently studied by Pontecorvo[24] in rhodium and by Segrè, Halford and Seaborg[24a] in bromine, because the absorption curves give no definite indication of the presence of a line spectrum of soft electrons.[25] This might make it appear that the two activities, arising from two different states of Zn^{69}, each decay by beta-emission to stable Ga^{69}. If there is a transition between the two levels of Zn^{69}, it has not been observed as a line of electrons in these experiments. However, the active samples were covered with Cellophane of three mg per cm^2 thickness (to protect the electroscope from contamination), so that very soft electrons would have been missed.

Radioactive Isotope Zn^{65}: From Zn+D, Cu+D and Cu+H; Half-Life 250 ± 5 Days (+ and K Electron Capture)

Perrier, Santangelo and Segrè have obtained[14] a radioactive zinc isotope with half-life 245 days from deuteron activated copper, by using filings from the copper deflector plate of the Berkeley cyclotron. The sign of the particles was not determined but they suggested the reaction $Cu^{63}(d, \gamma)Zn^{65}$; alternative possibilities for the transmutation are $Cu^{65}(d, 2n)Zn^{65}$ or $Cu^{63}(d, 2n)Zn^{63}$, with positron emission or K electron capture postulated in all cases.

Barnes and Valley have found[15] an activity in proton bombarded copper, the half-life of which was about seven months. Both positrons and electrons were observed, with a high γ/β ratio.

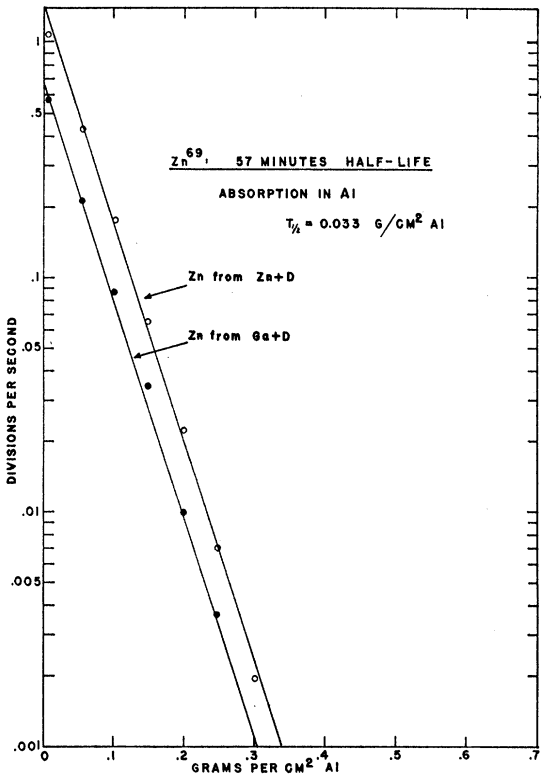

FIG. 4. Absorption curves of 57-minute period of Zn^{69}.

[22] E. E. Widdowson and F. C. Champion, Proc. Phys. Soc. **50**, 192 (1938).
[23] W. Gentner, J. de phys. et rad. **6**, 274 (1935).
[24] B. Pontecorvo, Phys. Rev. **54**, 542 (1938).
[24a] E. Segrè, R. S. Halford and G. T. Seaborg, Phys. Rev. **55**, 321 (1939).
[25] M. H. Hebb and G. E. Uhlenbeck, Physica V, 607 (1938).

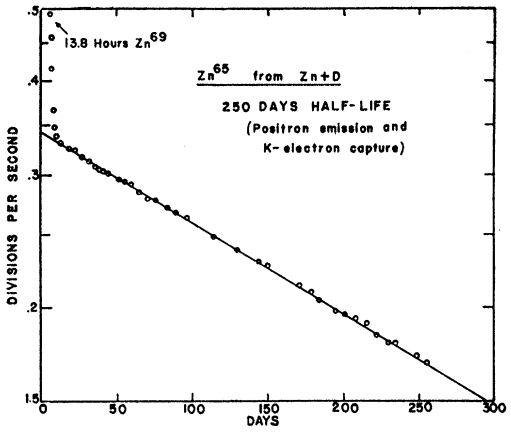

FIG. 5. Decay curve of Zn^{65}.

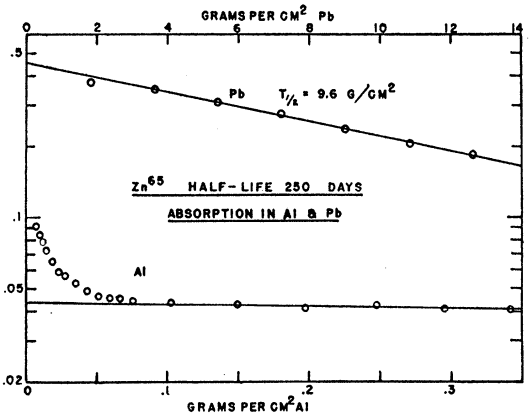

FIG. 6. Absorption curves of Zn^{65}.

This activity could be ascribed to either Zn^{65} or Zn^{63}, through the Cu(p, n)Zn reaction.

We have briefly announced[16] that the deuteron bombardment of zinc gives rise to a chemically identified zinc isotope with half-life of seven months, from which both positrons and electrons are observed. Since Zn^{63} cannot be produced by deuteron bombardment of zinc, the decay can now be assigned definitely to Zn^{65}; it is then necessary to postulate that the observed negative electrons are not of nuclear origin but are of a secondary nature. We will show that it appears likely that K electron capture occurs as an alternative to positron emission.

It seems certain that Zn^{65} has been produced in the following ways:

$$_{30}Zn^{64}+{}_1D^2\rightarrow{}_{30}Zn^{65}+{}_1H^1,$$
$$_{29}Cu^{65}+{}_1H^1\rightarrow{}_{30}Zn^{65}+{}_0n^1,$$

and either

$$_{29}Cu^{65}+{}_1D^2\rightarrow{}_{30}Zn^{65}+2{}_0n^1$$

or

$$_{29}Cu^{63}+{}_1D^2\rightarrow{}_{30}Zn^{65}+\gamma,$$

followed by

$$\left.\begin{aligned}&{}_{30}Zn^{65}\rightarrow{}_{29}Cu^{65}+{}_{+1}e^0\\ \text{and}\quad&{}_{30}Zn^{65}+{}_{-1}e^0\rightarrow{}_{29}Cu^{65}\end{aligned}\right\}\ 250\text{ days.}$$

Figure 5, displaying the decay of zinc precipitated from a bombardment of zinc with eight-Mev deuterons, shows the abrupt change of slope as the predominant activity changes from the 13.8-hour to the 250-day period. There is no trace of the 30-day decay quoted by Thornton.

Figure 6 exhibits the absorption curves of the 250-day activity. When beta-particles and gamma-rays are present in equal numbers, the ionization due to the particles is usually 30 to 70 times as much as that due to the gamma-rays. In this case, however, the gamma-ray causes more ionization than does the soft component. The presence of such a relatively small number of particles suggests at once that most of the transformations of Zn^{65} to Cu^{65} must occur as the result of the capture by Zn^{65} of one of its K electrons. The gamma-rays are emitted by the nucleus of Cu^{65} and are only slightly internally converted. The Cu $K\alpha$ x-ray line should also be present, emitted when the vacancy in the K shell is filled.

In one experiment, all of the particles were removed by a magnetic field between the specimen and the electroscope, and an absorption curve in aluminum was taken; this showed the presence of x-rays with approximately the absorption coefficient appropriate to the Cu $K\alpha$ line. A precise demonstration that the radiation actually is Cu $K\alpha$ would consist in showing that the absorption shows a discontinuity in the neighboring elements cobalt and nickel: Cu $K\alpha$ is strongly absorbed in cobalt and only weakly in nickel. This experiment was not attempted because sufficiently thin foils of cobalt were not available.

Alvarez[26] has also made x-ray absorption measurements on this activity. He found that the radiation could not be Zn $K\alpha$ since there

[26] L. W. Alvarez, Phys. Rev. **54**, 486 (1938).

was no large difference in the absorption in nickel and copper. The magnitude of his experimentally determined absorption coefficients showed that the x-rays were from an element in this region but of atomic number less than that of zinc; since they could not reasonably be from nickel, they must be copper $K\alpha$ radiation.

The soft component in Fig. 6 consists of x-rays and secondary electrons as well as positrons; for this reason it is not possible to give a value for the upper energy limit for the positrons from these data. Barnes and Valley, from cloud-chamber measurements, give a range of 0.20 gram per cm^2 Al, corresponding to an energy of about 0.7 Mev.

The absorption curve in lead shows the gamma-ray to be reduced to half-value by 9.6 grams per cm^2 Pb, which indicates an energy of 1.0 Mev. The fact that the 0.5-Mev annihilation radiation is present to an inappreciable amount lends confirmation to the conclusion that most of the Zn^{65} atoms decay by K electron capture rather than by positron emission.

In an earlier paper[21] one of us reported an activity of 130 days half-life in deuteron-activated copper, after following the decay for three months. Continued observations for two years have shown the period to lengthen out to 222 days, so that the activity is doubtless that of Zn^{65}, formed in the same manner as when reported by Perrier *et al.*, but contaminated with some shorter lived impurity.

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The Emission of Secondary Electrons Under High Energy Positive Ion Bombardment

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The yield of secondary electrons from metallic surfaces produced by high energy positive ions has been measured for the energy range 43 to 426 kv. Cold targets of Mo, Pb, Al and Cu were bombarded by protons, H_2^+ ions and He^+ ions. For protons the yield decreased from approximately 4 at low energies to approximately 2 at high energies. For H_2^+ ions the yields were more nearly constant with energy and about equal to 6. No great dependence of the yield on the kind of metal used was detected. The yield of secondaries from Mo under He^+ bombardment was approximately 13 and varied very slowly with the energy. The great majority of the secondaries had energies less than 30 volts in all cases. The electrostatic generator and associated high voltage apparatus is of a type which has been described before. However, several new features in the design and operation are described in detail here. The proton source is of the low voltage, capillary type and delivers 50 μa of focused ions of which approximately 50 percent are protons. This arc has been in operation for a year without replacement.

INTRODUCTION

THE emission of secondary electrons from metallic surfaces bombarded by positive ions has been studied in detail by several investigators in the range below 2000 volts energy. Representative examples are given by the work of Oliphant and Moon[1] in which molybdenum was bombarded by singly charged helium ions, and the work of Healea and Chaffee,[2] in which nickel was bombarded by hydrogen molecular ions. In the region of higher energies there is the work of Linford,[3] who used mercury ions, and the recently announced work of Allen,[4] with protons.

It is the purpose of the present work to investigate the yield of secondary electrons from several

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[1] M. L. E. Oliphant and P. B. Moon, Proc. Roy. Soc. **A127**, 373 (1930).

[2] M. Healea and E. L. Chaffee, Phys. Rev. **49**, 925 (1936).

[3] L. H. Linford, Phys. Rev. **47**, 279 (1935).

[4] J. S. Allen, Bull. Am. Phys. Soc. **13**, No. 5, Abs. No. 17 (1938).