The Induced Radioactivity of Calcium*

HAROLD WALKE†
University of California, Berkeley, California
(Received January 27, 1937)

A study has been made of the radioactivities induced in calcium by bombardment with high energy deuterons, alpha-particles and neutrons. Following irradiation by deuterons, the active samples have been separated chemically into fractions containing scandium, calcium and potassium. Most of the activity was found in the scandium precipitate, the decay curve of which has been analyzed into three components with half-lives of 53 ± 3 minutes, 4.0 ± 0.1 hours, and 52 ± 2 hours. The thick target yields of these active isotopes computed for an infinite duration of bombardment are 5.4×10^7, 3.6×10^7 and 3×10^8 deuterons per active atom. It is suggested that these periods are to be associated with Sc^{44}, Sc^{43} and Sc^{41}, respectively. The active calcium has been found to be due to Ca^{45}, the half-life of which is 2.4 ± 0.2 hours. The thick target yield of this isotope is approximately 9.0×10^8 deuterons per active atom. The 4-hour period has been identified with Sc^{43}, as the intense activity observed when calcium was bombarded with 0.2 microampere of 11 Mev alpha-particles decays with a single period of this value. The yield of Sc^{43} in this reaction is one active atom for 2×10^5 alpha-particles. Ca^{45} has also been produced by activating calcium with slow neutrons and by bombarding titanium with fast neutrons. It is shown that the 16-hour period previously reported was probably due to magnesium or sodium impurity and not to the formation of K^{42}, as the period of this isotope has been found to be 12.2 ± 0.2 hours.

INTRODUCTION

THE isotopes of calcium as given by Aston[1] are as follows:

Mass number	40	42	43	44
Percentage abundance	96.76	0.77	0.17	2.30

As recent work has shown that reactions of the type

$$_zA^N + {}_1H^2 \rightarrow {}_zA^{N+1} + {}_1H^1$$

in which the neutron of the deuteron is captured by the bombarded nucleus (the Oppenheimer-Phillips[2] reaction) are very probable among the elements of medium atomic number, it was anticipated that under bombardment by high speed deuterons the radioactive isotopes Ca^{41} and Ca^{45} would be formed, the former decaying to the stable K^{41} by positron emission and the latter emitting negative electrons to form Sc^{45}. The investigation to be discussed was carried out in order to search for Ca^{41}, for it was thought that a proof that this isotope is positron radioactive would preclude K^{41} as the source of the natural radioactivity of potassium.

APPARATUS

The cyclotron in the radiation laboratory was used as a source of deuterons, alpha-particles and neutrons. The deuterons of 5.5 Mev energy can now be passed into a bombarding chamber which is outside of the wall of the cyclotron and by means of a vacuum gate it is possible to bombard the water-cooled targets without causing the beam of ions to pass through a platinum window. In consequence the actual current arriving at the target has been increased by 50 percent and the total current measured can now be used for activation. In the experiments to be described the bombarding currents varied from 5 to 20 microamperes.

The alpha-particles were produced by replacing the deuterium in the chamber by helium and accelerating the doubly ionized helium ions. In this way a current of 0.2 to 0.3 microampere of alpha-particles with 11 million volts energy was obtained. It is of interest to point out that this current corresponds to the total number of alpha-particles emitted by approximately 4.5 grams of pure radium.

The neutrons were produced by allowing the deuteron beam to fall on a target of pure beryllium. With the new target chamber it is possible to place samples within a few inches of the bombarded beryllium. In consequence a very powerful neutron source was used corresponding to about 10^5 curies of radon plus beryllium. Slow neutron effects were observed by enclosing samples in thick blocks of paraffin wax while fast neutron activities were produced by placing

* Presented before the Physical Society, Pasadena Meeting, Dec. 1936.
† Commonwealth Fund Fellow.
[1] Aston, Proc. Roy. Soc. **A149**, 396 (1935).
[2] Oppenheimer and Phillips, Phys. Rev. **48**, 500 (1935).

the samples in a cadmium box which was surrounded with boron and lithium compounds.

All the observations of the decay of the active bodies were carried out with a Lauritsen type quartz fiber electroscope. Absorption measurements were made by placing aluminum sheets between the source and the window of the electroscope. The experimental points shown on the various curves have all been corrected for the natural leak of the electroscope.

Activation by Deuterons

Preliminary experiments with calcium fluoride targets had shown that the radioactivity induced in calcium by deuteron bombardment is complex in character. Accordingly, in recent experiments, calcite crystals and calcium metal, following activation, have been separated chemically into three fractions containing scandium, calcium and potassium.

Chemical separation

The following procedure[3] was used. The activated target was dissolved in dilute hydrochloric acid, the resulting solution being boiled to expel F^{17}, N^{13}, etc. Excess of ammonium chloride was added to prevent as far as possible the precipitation of calcium as hydroxide in the separation of scandium. A small quantity of aluminum nitrate solution was added, followed by excess of ammonia. The scandium and aluminum were thus precipitated as hydroxides. The precipitate was filtered off and washed thoroughly with ammonia and ammonium chloride solution.

The filtrate was boiled and sodium oxalate gradually added. The precipitated calcium oxalate was filtered off and washed with warm ammonium oxalate (in which scandium oxalate is soluble). The second filtrate was then heated with bromine water until the remaining ammonia was expelled as nitrogen. Finally a little potassium chloride was added and potassium precipitated by the addition of sodium cobaltinitrite reagent.

It was found difficult to separate the potassium free of calcium, as the calcium oxalate precipitate was usually very finely divided and passed through the filter paper. This difficulty has recently been overcome by the use of a very hard filter paper.

As a result of such chemical separations it has been established that most of the activity is due to scandium isotopes.

Decay of the calcium precipitate

The relatively weak calcium activity (intensity $1\frac{1}{2}$ hours after activation 0.05 of the scandium activity) decays with a period of about 2.4 hours. The thick target yield computed for equilibrium by correcting for the finite length of the bombardment is 9.0×10^8 deuterons per active atom. (Due to several uncertainties, such as the calibration of the electroscope, fluctuations in the bombarding current, etc., values of the yields of active atoms given are somewhat approximate.)

There is, in addition, a trace of a longer period, the initial intensity of which is little greater than the natural leak of the electroscope. On account of statistical fluctuations observations of such a weak activity are difficult to make. However, they have been made and it seems not at all unlikely that it is due to a small amount of scandium contamination, as the period would appear to be of the order 50–90 hours. The initial intensity of this period corresponds to about one percent of the total calcium activity.

By deflecting the particles emitted from the calcium fraction in a magnetic field[4] it has been found that they are negatively charged. Visual observation using a Wilson chamber and a magnetic field have confirmed this fact, though the occurrence of an occasional low energy positron is not precluded. These are probably due to the trace of scandium contamination. Gamma-rays are also emitted, rough absorption measurements in aluminum suggesting that these have an energy less than 0.5 Mev. The absorption curve shows, however, that the range of the electrons in aluminum is 0.89 g/cm^2 so that by Feather's rule their maximum energy is approximately 1.9 Mev.

Thus the radioactive calcium isotope is probably Ca^{45} produced by the reaction:

$$Ca^{44}+H^2\rightarrow Ca^{45}+H^1$$

[3] I am grateful to Dr. W. Libby for suggesting this procedure.

[4] I wish to thank Dr. A. H. Snell for assistance with this experiment.

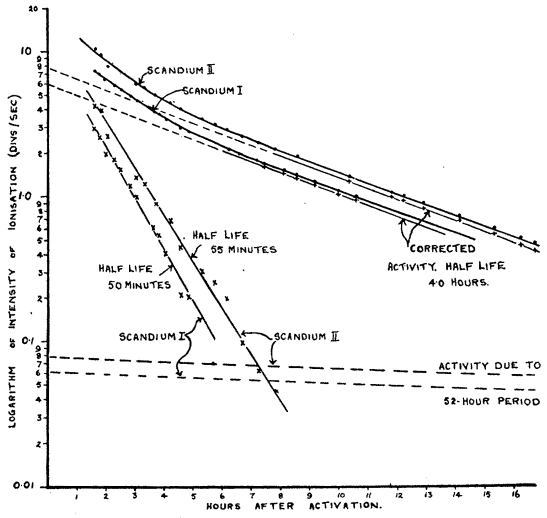

FIG. 1. Decay curves of active scandium separated from calcite crystals after irradiation with deuterons. The points indicated thus: · represent the total activity. Those marked + have been corrected for the activity due to the 52-hour period and the x's are the values obtained after subtraction of both the 52-hour and the 4-hour activities.

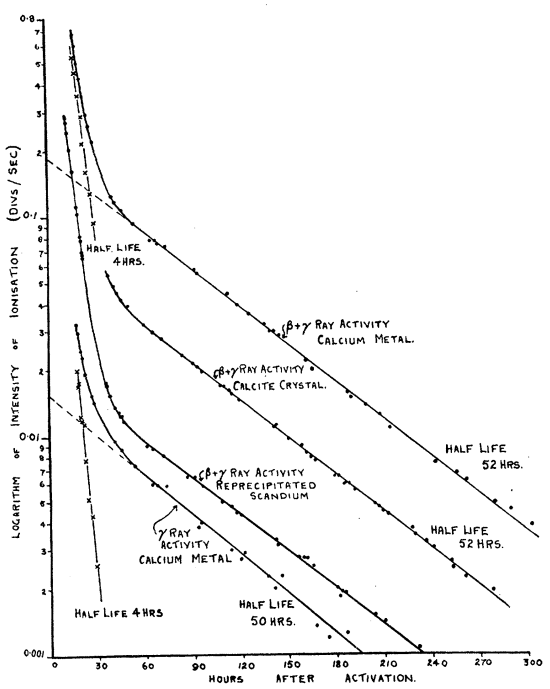

FIG. 2. Decay curves of long period activities of various scandium precipitates from calcium activated by deuterons. The x's are the values obtained after subtraction of the corresponding 52-hour activity.

and decaying with a half-life of 2.4 ± 0.2 hours to form the only known stable scandium isotope.

No definite evidence of positrons due to Ca^{41} has been obtained. In view of the very great abundance of Ca^{40} and the high probability of the formation of Ca^{41} by the Oppenheimer-Phillips type of reaction

$$Ca^{40}+H^2\rightarrow Ca^{41}+H^1,$$

this negative result suggests that Ca^{41} is either only just unstable, so that its half-life is very long, or on the other hand, that it is so short lived that its activity has not been detected.

Decay of the scandium precipitate

The decay of the very active scandium precipitate has been observed for more than 300 hours. The curve obtained is readily divisible into three well-defined parts with periods of 53 ± 3 minutes, 4.0 ± 0.1 hours, and 52 ± 2 hours. In Fig. 1 are shown the earlier portions of two such decay curves and it can be seen that there are two periods with half-lives of 4.0 hours and about 53 minutes. The value of the short period is not easily determined accurately on account of having to correct for the two longer periods. In Fig. 2 are shown decay curves of the long period activity. The gamma-ray decay was observed by placing aluminum 0.39 cm in thickness between the active sample and the electroscope window.

The thick target saturation yields corrected for the finite time of bombardment are as follows:

HALF-LIFE	YIELD (Deuterons per active atom)
53 ± 3 minutes	5.4×10^7
4.0 ± 0.1 hours	3.6×10^7
52 ± 2 hours	3.0×10^8

Absorption measurements were made 0.5 hour and 13 hours after the chemical separation was complete. The absorption curves obtained are shown in Fig. 3. It can be seen that the short-lived isotope emits more penetrating beta-rays than the isotope associated with the 4-hour period. The approximate ranges of the beta-rays in aluminum are 0.82 g/cm² and 0.65 g/cm², respectively, corresponding by Feather's rule, to maximum energies of 1.8 Mev and 1.4 Mev. Cloud chamber observations[5] show that the

[5] I am indebted to Mr. L. J. Laslett and Dr. D. Hurst for help with these experiments.

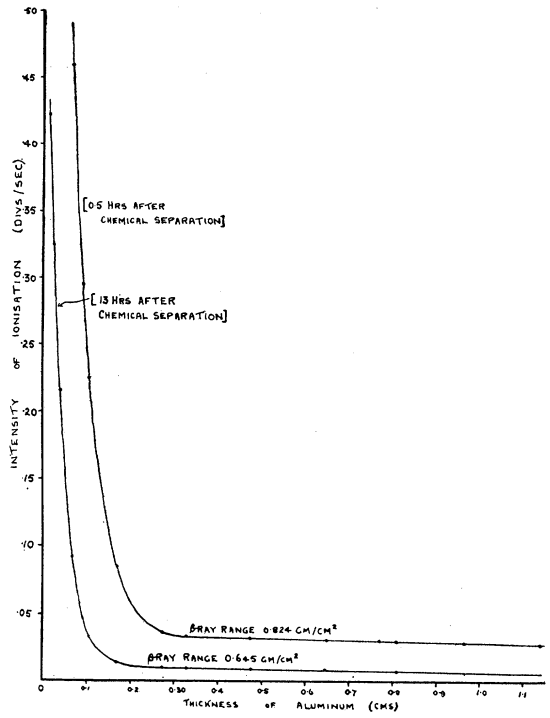

FIG. 3. Absorption curves of radiations emitted by radioactive scandium precipitates.

emitted particles are mainly positrons, though a few negative electrons were seen. The latter were probably due to Compton recoil electrons from the positron annihilation radiation and to a small amount of contamination from Ca^{45}.

In attempting to identify these radioactive bodies we may make use of the periods of already known unstable scandium isotopes. Zyw[6] has observed an induced radioactivity in potassium when bombarded with alpha-particles which decays to half value in 3 hours. As K^{39} is by far the most abundant isotope it is probable that the activity discovered by Zyw is due to Sc^{42} thus:

$$K^{39}+He^{4}\rightarrow Sc^{42}+n^{1}; \qquad Sc^{42}\rightarrow Ca^{42}+e^{+}.$$

Moreover, von Hevesy[7] has observed a very long lived scandium isotope Sc^{46} when scandium is activated with slow neutrons. The half-life is quoted[8] as being greater than a year.

As the formation of these isotopes under deuteron bombardment would involve the improbable reactions:

$$Ca^{40,\,44}+H^{2}\rightarrow Sc^{42,\,46}+\gamma,$$

in which radiative capture of the deuteron occurred, and as these periods do not agree with the three observed, it seems likely that the deuteron induced radioactivities are due to Sc^{41}, Sc^{43} and Sc^{44} formed by the reactions:

$$Ca^{40,\,42,\,43}+H^{2}\rightarrow Sc^{41,\,43,\,44}+n^{1}, \qquad (I)$$

in which the stable calcium isotopes capture the proton of the deuteron to give rise to the unstable scandium isotopes. As will be shown later the 4-hour period is due to Sc^{43}.

The question of Sc^{41} is of interest, for one would expect that it would decay thus:

$$Sc^{41}\rightarrow Ca^{41}+e^{+}; \qquad Ca^{41}\rightarrow K^{41}+e^{+},$$

resulting in two successive positron emissions and the formation of the unstable Ca^{41} which would then decay to form the only known stable isotope with the mass number 41, K^{41}. Thus one would anticipate that a radioactive calcium isotope would grow in the scandium precipitate. However, no evidence for the decay of Ca^{41} was obtained from the calcium precipitate and no activity could be detected in a calcium oxalate precipitate formed by adding a little inactive calcium chloride to a portion of the original scandium precipitate which had decayed for 14 hours and which was dissolved in dilute hydrochloric acid. Moreover, the reprecipitated scandium decayed in the same manner as the sample which had not been so treated (see Fig. 2.)

Professor Oppenheimer has pointed out that the reaction

$$Ca^{40}+H^{2}\rightarrow Ca^{41}+H^{1}$$

is a very probable one. The fact that no evidence of the decay of this isotope has been observed suggests that it is either nearly stable and of long half-life or so short lived as not to be detectable. The relatively high intensity of the 52-hour period could be explained if this period were associated with Sc^{41} formed thus:

$$Ca^{40}+H^{2}\rightarrow Sc^{41}+n^{1},$$

which then decayed to give the as yet undetected Ca^{41}. The short period of 53 minutes would then be associated with Sc^{44}. Summarizing we may

[6] Zyw, Nature **134**, 64 (1934).
[7] von Hevesy, Nature **135**, 1051 (1935).
[8] Rasetti, *Elements of Nuclear Physics* (Prentice-Hall, 1936), p. 273.

say that there are three periods associated with the scandium precipitate separated chemically from calcium after activation with 5.5 Mev deuterons with half-lives of 53 ± 3 minutes, 4.0 ± 0.1 hours and 52 ± 2 hours. The 4-hour period is due to Sc^{43}, the other periods being probably due to Sc^{44} and Sc^{41} formed by reactions (I).*

Decay of the potassium precipitate

The radioactivity associated with the potassium precipitate is usually masked by contamination of Ca^{45}. Moreover, a sample which showed merely a trace of such short period was only weakly active, the corrected intensity 9 hours after activation being only three times as great as the natural leak of the electroscope. However, the observations fit fairly well a single straight line corresponding to a half-life of 10.5 hours. The intensity of the activity is so small that it may be due to a small amount of some impurity. As, however, the period does not agree with that of any well-known contaminant, it is possible that this radioactive body is an isotope of potassium, in which case it is probably K^{38} produced thus:

$$Ca^{40}+H^2\rightarrow K^{38}+He^4; \qquad K^{38}\rightarrow A^{38}+e^+$$

and decaying by emitting positrons to form A^{38}. The only other radioactive potassium isotope which could be produced is K^{42} by the reaction

$$Ca^{44}+H^2\rightarrow K^{42}+He^4; \qquad K^{42}\rightarrow Ca^{42}+e^-;$$

* *Note added in proof.* Recently radioactive scandium has been separated chemically from potassium fluoride after bombardment with 0.1 microampere of 11 Mev alpha-particles. By deflecting the emitted particles in a magnetic field it has been established that they are positrons. The decay curve shows the presence of two isotopes with half-lives of 4.1 ± 0.2 hours and 52 ± 2 hours. As the long period agrees with that observed in the scandium precipitate from calcium + deuterons it must be associated with Sc^{44} thus:

$$Ca^{43}+H^2\rightarrow Sc^{44}+n^1;\ Sc^{44}\rightarrow Ca^{44}+e^+$$
$$K^{41}+He^4\rightarrow Sc^{44}+n^1.$$

The 4.1 hour period is then due to Sc^{42} produced by the reaction:

$$K^{39}+He^4\rightarrow Sc^{42}+n^1;\ Sc^{42}\rightarrow Ca^{42}+e^+.$$

Thus we have:

Radioactive isotope	Half-life
Sc^{41}	$53\ \pm3$ minutes
Sc^{42}	4.1 ± 0.2 hours
Sc^{43}	4.0 ± 0.1 hours
Sc^{44}	$52\ \pm2$ hours

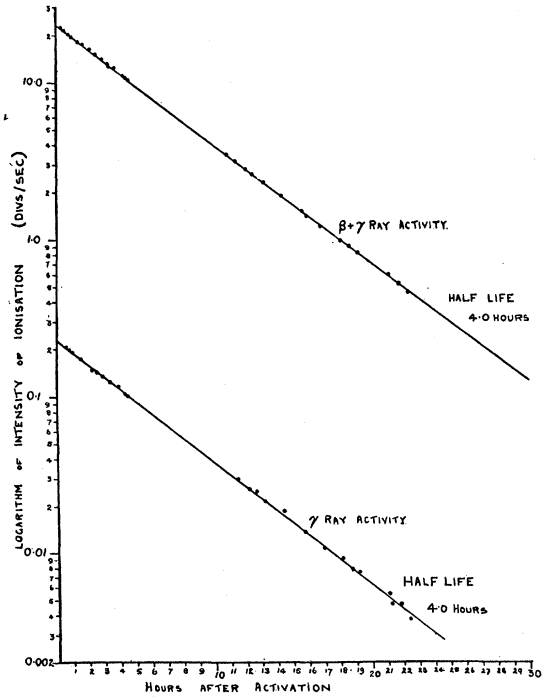

FIG. 4. Decay curve of calcium metal after activation by alpha-particles.

but as will be discussed later the half-life of this isotope is 12.2 hours.

ACTIVATION BY ALPHA-PARTICLES

Frisch[9] has bombarded calcium with a alpha-particles and has detected an induced radioactivity, the decay period of which he reported as "4.4 hours with a possible error of 10 percent." He showed that the particles emitted were positrons and from their intensity deduced that the effect was due to Ca^{40}. Chemical tests proved that the active isotope followed the reactions of scandium and he concluded that the activity was due to Sc^{43}. This has been confirmed by Pollard and Brasefield[10] who have detected the protons emitted in the reaction

$$Ca^{40}+He^4\rightarrow Sc^{43}+H^1.$$

The period given by Frisch[9] agrees within the limits of error with the 4-hour period observed with deuterons. It has recently been proved that the two radioactive isotopes are

[9] Frisch, Nature **136**, 220 (1935).
[10] Pollard and Brasefield, Phys. Rev. **51**, 8 (1937).

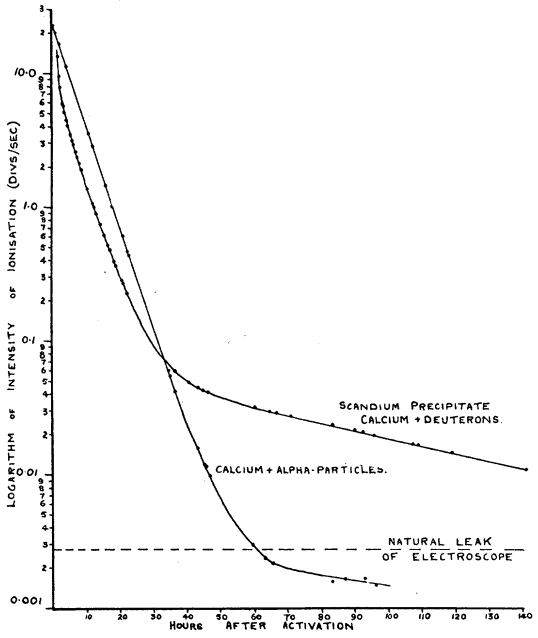

FIG. 5. Comparison between alpha-particle and deuteron induced activities.

identical by repeating Frisch's experiments using the artificially accelerated alpha-particles with 11 million volts energy. A sample of calcium metal was bombarded for about half an hour with 0.2 microampere of the ions and was found to be extremely active (initial intensity $10^5\times$the natural leak of the electroscope). The activity decayed with a single period the half-life of which is 4.0 hours with an accuracy of about 1–2 percent. The decay curve is shown in Fig. 4.

The thick target saturation yield corrected for the finite period of bombardment is 2×10^5 alpha-particles per active atom.

Absorption measurements show the emitted positrons to have the same range in aluminum as those ejected by the active isotope with the 4-hour period formed by the deuteron activation. It is thus clear that Sc^{43} has been produced by the two reactions:

$$Ca^{42}+H^2\rightarrow Sc^{43}+n^1; \qquad Sc^{43}\rightarrow Ca^{43}+e^+,$$
$$Ca^{40}+He^4\rightarrow Sc^{43}+H^1,$$

its half-life being 4.0 ± 0.1 hours.

There was very little contamination of the alpha-particle beam by deuterons as can be seen from Fig. 5 which shows a comparison between the decay of the deuteron and alpha-particle induced activities. There is evidence of a very weak longer period, the initial intensity of which is 1/100,000 of the initial total intensity. It is probable that this is due to deuterons, though there is no trace of the corresponding short period.

ACTIVATION BY NEUTRONS

Fermi and his co-workers[11] irradiated CaF_2 in water for 14 hours using a strong source of neutrons consisting of 600 millicuries of radon mixed with beryllium but failed to detect any induced radioactivity. On the other hand, Hevesy and Levi[12] irradiated calcium carbonate with neutrons and observed two periods of 4 hours and 16 hours, respectively. In the chemical separation they added sodium chloride to the solution formed by dissolving the irradiated calcium carbonate in dilute hydrochloric acid and after precipitating the calcium as oxalate found the 16-hour activity in the sodium chloride filtrate. The low intensity of the activity they ascribed to the low abundance of Ca^{42}, the reaction postulated being:

$$Ca^{42}+n^1\rightarrow K^{42}+H^1; \qquad K^{42}\rightarrow Ca^{42}+e^-.$$

The author has repeated these experiments on calcium carbonate and has observed such a weak activity. The decay curve obtained is shown in Fig. 6 and is divisible into two portions. The value of the long period, however, was found to be 14.5 hours (corresponding to the 16-hour period reported by Hevesy and Levi[12]) and this is so close to the half-life of Na^{24} (14.8

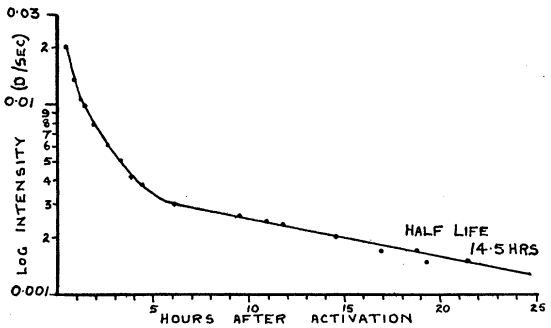

FIG. 6. Decay curve of calcium carbonate following activation by neutrons.

[11] Fermi *et al.*, Proc. Roy. Soc. **A149**, 522 (1935).
[12] Hevesy and Levi, Nature **135**, 580 (1935).

hours[13]) that it is very probably due to the presence of this isotope formed from sodium or magnesium contamination thus:

$$Na^{23}+n^1\rightarrow Na^{24}+\gamma; \qquad Na^{24}\rightarrow Mg^{24}+e^-,$$
$$Mg^{24}+n^1\rightarrow Na^{24}+H^1.$$

The activity is certainly not due to K^{42}, for three samples of potassium salts irradiated with slow neutrons were made strongly radioactive, the decay curves being excellent straight lines corresponding to a half-life of 12.2 ± 0.2 hours.

Calcium metal

On the other hand two samples of calcium metal from different sources when strongly irradiated with slow neutrons were rendered active and, as shown in Fig. 7, the radioactive isotope decays to half-value in 2.4 ± 0.2 hours in agreement with the period of Ca^{45} formed by deuteron bombardment. It was established that this period is not due to silicon present as impurity, for samples of silicic acid were irradiated at the same time and under the same conditions and as can be seen from Fig. 7 the activity induced is only one-fifth as intense as in the calcium. Moreover, the period of Ca^{45}, 2.4 ± 0.2 hours is less than that of Si^{31}, 2.7 ± 0.2 hours.

The weak short-lived activity observed has a half-life close to 30 minutes and may be due to a fast neutron reaction. On the other hand, as the calcium metal was cleaned with hydrochloric acid, this may be due to traces of chlorine contamination. This seems likely, for when calcium metal was bombarded with fast neutrons only a very weak activity was observed, the initial intensity of which was three times as great as the natural leak of the electroscope. There was evidence for a short period, but the shape of the decay curve is such that the activity may well be due to a small number of slow neutrons. There is no evidence for a 12-hour period, which suggests that if the reaction proposed by Hevesy,[12] *viz.*

$$Ca^{42}+n^1\rightarrow K^{42}+H^1$$

occurs at all the resultant activity is so weak that it has not yet been observed.

However, the possibility that the short period is due to a fast neutron disintegration of calcium is not definitely excluded.

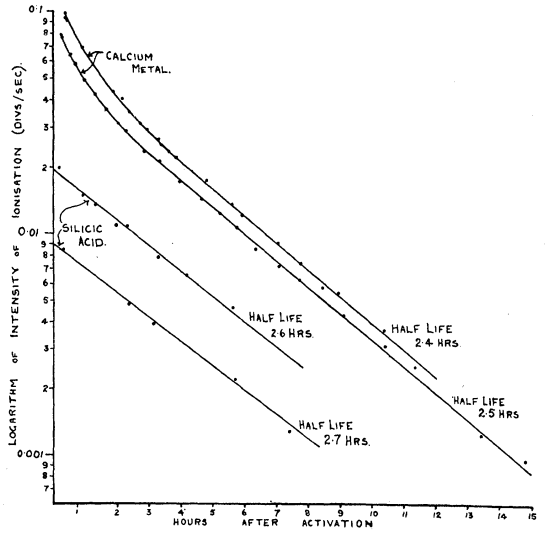

FIG. 7. Decay curves of calcium metal after irradiation with slow neutrons.

Titanium metal

Further evidence confirming the half-life of Ca^{45} has been obtained by bombarding titanium metal with fast neutrons. An analysis of the decay curve of the radioactivity induced shows the presence of a very short period, probably due to Ti^{51} (half-life 3.0 minutes[9]) together with a new period of 2.3 hours which agrees with the half-life of Ca^{45}. As the most abundant isotope of titanium, Ti^{48}, is present to an extent of 78 percent, it appears probable that the reaction:

$$Ti^{48}+n^1\rightarrow Ca^{45}+He^4$$

has been detected.

ACKNOWLEDGMENTS

The author is very greatly indebted to Professor E. O. Lawrence both for the privilege of working in the radiation laboratory and for his continued encouragement. Moreover, it gives the author pleasure to express his appreciation of the friendship and cooperation of the staff of the radiation laboratory and he thanks them for valuable suggestions and discussions. The experimental work has been aided by grants from the Research Corporation, the Chemical Foundation and the Josiah Macy Jr. Foundation.

[13] Van Voorhis, Phys. Rev. **49**, 889 (1936).