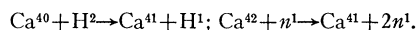


## The Radioactive Isotopes of Calcium and Their Suitability as Indicators in Biological Investigations

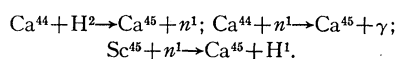
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(Received November 28, 1939)

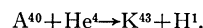
A further study of the induced radioactivity of calcium has been made. It has been established that the 2.5-hour period previously assigned to  $\text{Ca}^{45}$  is in fact associated with  $\text{Ca}^{49}$ . It is shown that this isotope probably exists in two isomeric forms with half-lives  $30 \pm 1$  min. and  $2.5 \pm 0.1$  hours. The growth of  $\text{Sc}^{49}$  of half-life  $57 \pm 2$  min. from the 2.5-hour form of  $\text{Ca}^{49}$  has been observed. The maximum energy of the electrons emitted by  $\text{Ca}^{49}$  (2.5-hour period) is  $2.3 \pm 0.1$  Mev, the end point at  $1.8 \pm 0.1$  Mev being probably due to the  $\text{Sc}^{49}$  in equilibrium with its parent.  $\gamma$ -rays of energy  $0.8 \pm 0.1$  Mev are emitted by  $\text{Ca}^{49}$  (2.5-hour period).  $\text{Ca}^{41}$  of half-life  $8.5 \pm 0.8$  days decays by  $K$ -electron capture. A  $\gamma$ -ray of energy  $1.1 \pm 0.1$  Mev is emitted and is internally converted to an extent of  $\sim 10^{-3}$ .  $\text{Ca}^{41}$  has been produced by the reactions



$\text{Ca}^{45}$  of half-life  $180 \pm 10$  days emits electrons of energy  $0.19 \pm 0.01$  Mev (95 percent) and  $0.91 \pm 0.03$  Mev (5 percent) and  $\gamma$ -radiation of energy  $0.71 \pm 0.03$  Mev. Its formation has been observed in the following reactions:



The suitability of these isotopes as radioactive indicators is discussed, and it is concluded that  $\text{Ca}^{45}$  is likely to prove the only useful one. By bombarding calcium with fast neutrons, a radioactivity of half-life  $4.5 \pm 0.5$  min. has been confirmed, but not identified. No radioactive isotopes of potassium of long half-life have been extracted from calcium by activation with fast neutrons, nor has any evidence been obtained for the reaction



### INTRODUCTION

IN biological investigations radioactive isotopes of long half-life are generally to be preferred since in most cases the processes to be studied occur at a relatively slow rate. However, isotopes with short half-lives (from 20 minutes to a few hours) may be successfully used if they can be produced in sufficient intensity. Thus, already experiments have been attempted using the radioactive calcium of half-life 2.5 hours previously detected by one of us (H. W.) in calcium metal which had been bombarded with deuterons of high energy. However, very active samples of this body are not easy to prepare so that it seemed pertinent to make a careful search for other radioactive forms of calcium which might prove more suitable as indicators in investigations of calcium metabolic processes. It is the purpose of this paper to present the results of such a successful search and to discuss

the possibility of using the various active bodies in biological investigations.

The earlier experiments had been carried out using calcium which had been bombarded for 10–20 microampere hours with deuterons of energy 5.5 Mev. When currents of the order 100 microamperes of 8-Mev deuterons became available from the Berkeley cyclotron, it was thought worth while to reinvestigate the problem of radioactive calcium as it appeared likely that samples initially more active by a factor of twenty could be obtained which would render possible the discovery of radioactive isotopes of long half-life.

Professor Alvarez was kind enough to send us in Liverpool a piece of calcium metal which was bombarded in May, 1938, with deuterons of energy 8 Mev for 100 microampere hours and such long period activities have been observed and their properties studied in some detail. However, additional experiments have been necessary in order to identify the new bodies with certainty and these have been carried out by one of us (H.W.) working in the Radiation Laboratory of the University of California.

\* Exhibition of 1851 Senior Student. Present address George Holt Physics Laboratory, The University, Liverpool, England. Word of Dr. Walke's untimely death reached this country while this paper was in proof.

For convenience of reference, the stable isotopes referred to in the text are given in Table I.

#### APPARATUS

The general nature of the various radioactive bodies was investigated by means of the large expansion chamber designed by Williams<sup>1</sup> and used as described by Walke, Williams and Evans<sup>2</sup> in their investigations of V<sup>47</sup>, V<sup>48</sup>, Ti<sup>51</sup> and Sc<sup>46</sup>. This chamber has a large effective volume and a sensitive time of 0.4 sec. The radioactive sources to be investigated were placed inside the chamber, thus reducing to a minimum the absorption between the source and the region where tracks could be observed. The radioactive material was covered with a shutter which was timed to open during the sensitive period of the chamber. A magnetic field was used to determine the sign of the electrons emitted and also to clear the chamber of electron tracks when investigating x-radiation from the source. For the latter purpose the maximum field available, *viz.*, 2200 oersteds was used. This was sufficient to bend away all the electrons and thus give a clear background for any photoelectron tracks produced by x-rays. The x-radiation in the present investigation is the K radiation from potassium whose quantum energy is  $\sim 4500$  ev. The corresponding photoelectrons in air at atmospheric pressure have a very short range, appearing as spots in the photographs. The rate of decay of the long period positrons\* was obtained by

counting tracks on photographs taken at different intervals over a period of 6 months. In these measurements precautions were taken to ensure that the photographs were obtained under identical conditions in particular that the time (0.3 sec.) for which the shutter was open was the same throughout. This time was controlled by switches placed in the path of a falling weight and could be reproduced at long intervals with an accuracy of 0.01 sec.

The rate of decay of the various activities was obtained from measurements of the ionizations produced using a standard Lauritsen electro-scope. The electro-scope had a window of aluminum 0.0013 mm thick equivalent in stopping power for  $\beta$ -rays to about 4 mm of air.

The absorption in aluminum of the electrons emitted by the various sources was measured using as a detector a Geiger-Müller counter with a thin mica window and the arrangement described by Feather,<sup>3</sup> or a Lauritsen electro-scope.†

The quantum energy of the  $\gamma$ -rays emitted was obtained from measurements of the ranges in aluminum of their recoil electrons. The method adopted was the standard one of counting coincidences in two thin-walled counters between which aluminum foils could be placed, the recoil electrons being ejected from the wall of the counter near the source.

The radioactive materials were prepared with the 37-inch Berkeley cyclotron.

#### K-ELECTRON CAPTURE AND INTERNAL CONVERSION IN Ca<sup>41</sup>

From the early experiments no evidence was obtained for Ca<sup>41</sup> which was therefore assumed

production of Ca<sup>46</sup>.) It now seems probable that the positrons are due to Na<sup>22</sup> formed from a small percentage of magnesium present as impurity in the calcium, the reaction being  $Mg^{24} + H^2 \rightarrow Na^{22} + He^4$ . Thus, the half-life (determined with the cloud chamber)  $3.5 \pm 0.5$  years and the energy of the positrons  $0.50 \pm 0.05$  Mev agree reasonably well with the known values for Na<sup>22</sup> *viz.*  $3.0 \pm 0.2$  years and  $0.55 \pm 0.02$  Mev, respectively. Moreover,  $\gamma$ -radiation of energy  $1.4 \pm 0.1$  Mev has been observed which accords with the recently published figure  $1.3 \pm 0.1$  Mev given by Oppenheimer and Tomlinson. Finally, chemical analysis has shown that a long period activity can be separated with sodium after the careful removal of scandium, calcium and potassium. The amount of magnesium impurity necessary to account for the observed positrons is 0.4 percent which is not unreasonable for calcium metal.

<sup>3</sup> N. Feather, Proc. Camb. Phil. Soc. **34**, 599 (1938).

† Feather's (reference 3) range energy relation was used to calculate the energy of electrons  $> 0.7$  Mev. Below 0.7 Mev the relation for homogeneous  $\beta$ -rays was applied.

TABLE I. Stable isotopes to which reference is made in the text.

ELEMENT	MASS NUMBERS AND ABUNDANCE						
18A	36	38	40				
	0.308	0.061	100				
19K	39	40	41				
	100	0.012	7.15				
20Ca	40	42	43	44	46	48	
	100	0.66	0.15	2.13	0.0034	0.191	
21Sc	45						
	100						
22Ti	46	47	48	49	50		
	10.82	10.56	100	7.50	7.27		

<sup>1</sup> E. J. Williams, Proc. Roy. Soc. **A172**, 194 (1939).

<sup>2</sup> Walke, Williams and Evans, Proc. Roy. Soc. **A171**, 360 (1939).

\* Considerable attention has been devoted to the positrons of long half-life which were at first thought to be due to an isomeric form of Ca<sup>41</sup>. (It was noted, however, that the cross section for the formation of this body assuming the reaction to be  $Ca^{40} + H^2 \rightarrow Ca^{41} + H^1$  was smaller by a factor of 100 than the corresponding cross section for the

to have a very long or a very short half-life. Following the discovery of nuclear  $K$ -electron capture, however, it seemed more probable that the failure to observe this isotope was due to its decaying by  $K$  capture and thus emitting only very soft x-radiation which would make its activity very difficult to detect.

We therefore looked for the emission of x-rays from calcium metal which had been activated with deuterons using the large cloud chamber to detect the photoelectrons. After the 52-hour activity of  $\text{Sc}^{44}$  produced in the reaction  $\text{Ca}^{43}(\text{H}^2, n^1)\text{Sc}^{44}$  had decayed entirely the source was found to emit large numbers of low energy electrons, positrons, x-rays and a group of high energy electrons present in small intensity. Most of the soft electrons and positrons are emitted by activities of long half-life but the x-radiation decayed much more rapidly as did the group of high energy electrons. The cloud-chamber pictures suggested that the electrons were distinctly homogeneous in energy. This was confirmed by absorption measurements which showed in fact that they constituted a line of electrons of energy  $1.1 \pm 0.05$  Mev.

The decay of part of the sample and of calcium oxalate precipitates chemically separated from other portions were investigated with an electro-scope. The various samples decayed in the same fashion, the curves being complex; however, they could be analyzed into two components due to two radioactive isotopes of calcium with half-lives  $8.5 \pm 0.8$  days and  $180 \pm 10$  days, respectively.

The cloud-chamber observations showed that the energetic electrons and almost all the x-rays were absent when the 8.5-day activity had gone, though the majority of the positrons and soft electrons remained. The association of the electron line with the half-life 8.5 days was also established by absorption measurements. It was found in addition that a hard  $\gamma$ -ray of energy  $1.1 \pm 0.1$  Mev accompanied this activity.

The close agreement between the energy of the hard electrons and the  $\gamma$ -radiation suggested that the electrons are in fact produced by the internal conversion of the  $\gamma$ -ray. That this is very probable appears from the absorption curve shown in Fig. 1. The shape is quite different from that of a continuous spectrum of similar energy.

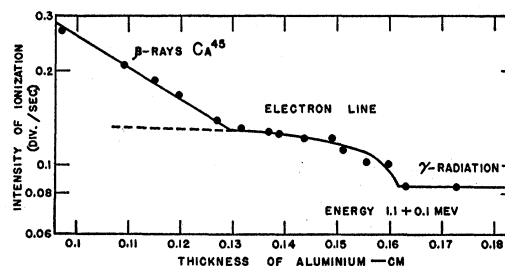


FIG. 1. Absorption curve showing electron line emitted by  $\text{Ca}^{41}$ .

However, the number of x-ray quanta emitted is greater than the number of conversion electrons by a large factor (precise ratios are unfortunately not at present available, though further studies are planned). The majority of the x-rays are therefore not produced by the internal conversion process but arise in some other manner, most probably by  $K$ -electron capture. It has not been possible to identify the atomic number of the emitting atom in this case because of the very low energy of the  $K$  radiation and the high background of  $\gamma$ -rays. But it seems likely that this 8.5-day activity is due to a form of  $\text{Ca}^{41}$  decaying by  $K$ -electron capture. In some cases the  $K$  electron is captured into the ground state of the product nucleus  $\text{K}^{41}$  but a considerable fraction of the  $\text{K}^{41}$  nuclei are left in an excited state 1.1 Mev above the ground state. The  $\gamma$ -radiation then emitted is internally converted and so gives rise to the electron line. The internal conversion coefficient of the  $\gamma$ -radiation has not yet been measured accurately but appears to be exceptionally high—most probably greater than 0.1 percent. This requires a large spin difference between the excited state and the ground state, a result which is rather unexpected. Quite similar results, however, have been obtained with  $\text{Cr}^{51}$  which has been more fully studied and will be reported in detail later.<sup>4</sup>

The excitation of the level at 1.1 Mev indicates that positron emission by this 8.5-day activity is energetically possible. However, the existence of positrons with this half-life has not been established with certainty. The majority of the emitted positrons have a half-life of about 3 years\* and a small effect due to the short period could easily have been missed.

<sup>4</sup> Walke, Thompson and Holt. To be published in the *Physical Review*.

\* See asterisk footnote on p. 178.

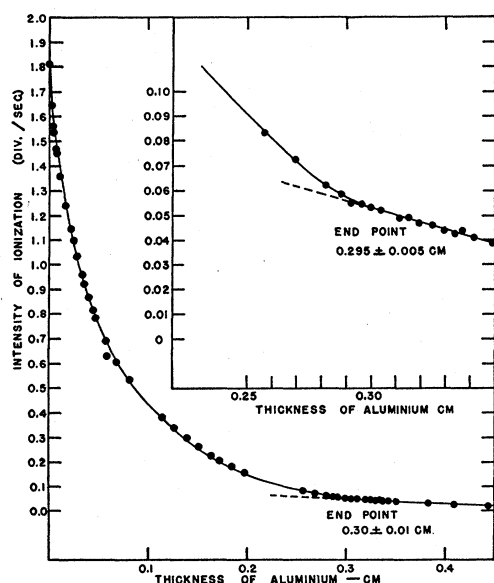
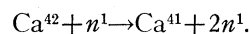


FIG. 2A. Absorption in aluminum of electrons emitted by  $\text{Ca}^{49}$ . The end point at 1.8 Mev is probably due to  $\text{Sc}^{49}$  in equilibrium with its 2.5-hour parent.

By subjecting spectroscopically pure calcium oxide to a prolonged bombardment with fast neutrons (700 microampere hours 8-Mev deuterons on beryllium), a weak activity of half-life  $8.5 \pm 1.0$  days has been observed. This is probably due to  $\text{Ca}^{41}$  formed in the reaction



This form of  $\text{Ca}^{41}$  would be quite unsuitable for biological work in spite of its convenient half-life because of the high absorption of the soft x-radiation which is the main radiation emitted.

#### ISOMERS OF $\text{Ca}^{49}$

The radioactive isotope of calcium of half-life 2.5 hours which can be produced by bombarding calcium with deuterons and slow neutrons emits negative electrons and  $\gamma$ -radiation. It was previously assumed to be  $\text{Ca}^{45}$ , the assignment being at that time unique, for no stable isotope of calcium of mass number greater than 44 was then known. The discovery by Nier that both  $\text{Ca}^{46}$  and  $\text{Ca}^{48}$  are stable made the assignment uncertain and suggested moreover that other radioactive calcium isotopes could be produced.

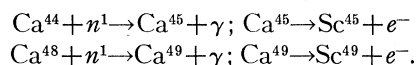
In this connection it may be noted that a 30-minute period was previously observed by one

of us (H. W.)<sup>5</sup> in calcium metal which had been activated with slow neutrons. It was then not closely investigated as it was thought to be due to chlorine contamination.

The short-lived activities induced in calcium by deuterons and slow neutrons have therefore been carefully reinvestigated using various calcium compounds as targets. In particular spectroscopically pure calcium oxide (Hilger 11814) has been extensively used for slow neutrons studies.

It has thus been established that the body of half-life 30 minutes previously assumed to be impurity is in fact a true activity which can be induced in calcium with slow neutrons and deuterons but not with fast neutrons. It has been chemically separated as calcium and its half-life measured with six different samples is  $30 \pm 1$  min.

Since negative electrons are emitted this radioactive isotope of calcium is probably to be associated with  $\text{Ca}^{45}$  or  $\text{Ca}^{49}$  produced according to the reactions



It cannot be a metastable isomer of a stable calcium isotope since it is produced by *slow* neutrons. However, as shown in a previous paper,  $\text{Sc}^{49}$  is itself  $\beta$ -radioactive with a half-life of  $57 \pm 2$  minutes. If, therefore, either of the calcium isotopes of half-lives 30 min. and 2.5 hours were  $\text{Ca}^{49}$  and thus the parent of the 57-minute  $\text{Sc}^{49}$  it should be possible to extract  $\text{Sc}^{49}$  from calcium which had been activated with slow neutrons.

Several experiments to test this point have been made, and it is indeed possible to produce strong sources of  $\text{Sc}^{49}$  in this way. The separated scandium was chemically purified very carefully (being reprecipitated in the presence of inactive calcium at least three times) and was observed to decay with a single period of  $57 \pm 2$  minutes. Moreover, by making successive extractions of scandium at intervals after activation had ceased it was established that certainly the body with half-life 2.5 hours is one parent of  $\text{Sc}^{49}$ . Thus  $\text{Sc}^{49}$  could be chemically extracted six hours after the sample had been initially freed

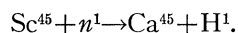
<sup>5</sup> H. Walke, Phys. Rev. **51**, 439 (1937).

from scandium, even when any  $\text{Sc}^{49}$  which might have resulted from the decay of the 30-minute body was carefully separated 2.5 hours previously.

The activity of half-life 2.5 hours previously assigned to  $\text{Ca}^{45}$  is then in fact due to  $\text{Ca}^{49}$ .

At present we cannot decide definitely whether or not the 57-minute period also grows from the calcium isotope of half-life 30 minutes since it has not yet been found possible to carry out the chemical separations sufficiently rapidly. The problem is complicated, moreover, by the fact that the intensity of the 30-minute activity is considerably less than that of the body of half-life 2.5 hours.

There is other evidence, however, which indicates that the 30-minute activity is an isomer of  $\text{Ca}^{49}$  rather than  $\text{Ca}^{45}$  since a number of experiments have clearly established that neither the 30-minute nor the 2.5-hour period can be produced by bombarding scandium with fast neutrons, though  $\text{Ca}^{45}$  (see next section) can be produced by the reaction.



In this connection it must be noted that the previous assignment of the 2.5-hour period to  $\text{Ca}^{45}$  appeared to be confirmed by the observation of an activity with quite similar half-life when titanium was bombarded with fast neutrons (reaction  $\text{Ti}^{48} + n^1 \rightarrow \text{Ca}^{45} + \text{He}^4$ ).<sup>6</sup> These experiments have been carefully repeated using high purity titanium donated by Messrs. N. V. Philips Gloeilampenfabrieken of Eindhoven, Holland,\* but no such 2.5-hour period has been observed. It is probable that the titanium used previously contained traces of iron or manganese impurity.

In the first report of the energy of the radiations emitted by the isotope of half-life 2.5 hours<sup>5</sup> the value given for the electrons was  $1.9 \pm 0.1$  Mev, the  $\gamma$ -rays being said to be softer than annihilation radiation. These measurements have been repeated by studying the absorption of the emitted radiation in aluminum and lead. The absorption curves for the electrons are shown in Figs. 2A and 2B. The "spectrum" is certainly

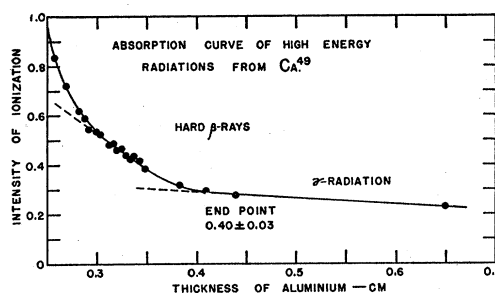


FIG. 2B. Absorption curve of radiations from  $\text{Ca}^{49}$  showing hard group of  $\beta$ -rays and  $\gamma$ -radiation.

complex, the previously assumed soft  $\gamma$ -rays being actually a group of  $\beta$ -particles of maximum energy  $2.3 \pm 0.1$  Mev. The end point at  $1.8 \pm 0.1$  Mev is very probably the upper limit of the spectrum due to the transformation product  $\text{Sc}^{49}$  ( $E = 1.8 \pm 0.1$  Mev).<sup>5</sup>

An interesting feature of the curve is the considerable intensity of low energy electrons which is somewhat unexpected for a  $\beta$ -spectrum with such a high upper limit. It is possible that these may be conversion electrons emitted in the  $\gamma$ -transition between isomeric states of  $\text{Ca}^{49}$ .

The  $\gamma$ -ray energy  $0.8 \pm 0.1$  Mev has been obtained from absorption measurements in lead.

Since the transformation product  $\text{Sc}^{49}$  is in equilibrium with the  $\text{Ca}^{49}$  of half-life 2.5 hours, it is apparent that the results of biological experiments using  $\text{Ca}^{49}$  would not be accurate. If, moreover, the 2.5-hour period should prove to be associated with the metastable form of  $\text{Ca}^{49}$ , then it is possible that some complex organic molecules containing  $\text{Ca}^{49}$  would be decomposed by the  $\gamma$ -decay (as in the case of bromine, tellurium, etc.  $\text{Ca}^{49}$  would, therefore, not be very suitable as an indicator in biological research.

#### LONG-LIVED $\text{Ca}^{45}$

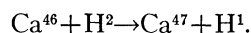
After the decay of the 8.5-day activity the majority of the particles emitted by calcium which has been activated with high speed deuterons are electrons of low energy ( $\sim 100,000$  ev). It has been established by a number of careful chemical analyses\* that these radiations are emitted by a radioactive isotope of calcium of half-life  $180 \pm 10$  days (Fig. 3).

<sup>6</sup> H. Walke, Phys. Rev. 52, 777 (1937).

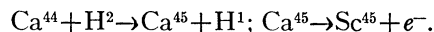
\* It is a pleasure to thank Messrs. N. V. Philips for making us this gift of high purity titanium metal.

\* See Appendix.

It is unlikely that this new isotope is  $\text{Ca}^{47}$  for the low abundance of the stable  $\text{Ca}^{47}$  (0.0034 percent) precludes the possibility of its formation by the reaction



Moreover,  $\text{Ca}^{47}$  would decay to  $\text{Sc}^{47}$  of half-life 63 hours, and this active body could be chemically separated from the  $\text{Ca}^{47}$  with which it would be in equilibrium. Repeated chemical analyses have proved, however, that no active scandium is produced by the decay of the 180-day activity. Since  $\text{Sc}^{45}$  is the only stable scandium isotope, it is, therefore, probable that this long-lived  $\beta$ -radioactive calcium isotope is  $\text{Ca}^{45}$  produced by the reaction:



The electrons emitted by  $\text{Ca}^{45}$  consist of two groups. The main group has a maximum energy of  $0.19 \pm 0.01$  Mev. The absorption in aluminum is shown in Fig. 4. The second more penetrating group of electrons is present to an extent of  $\sim 5$  percent and has a maximum energy of  $0.91 \pm 0.03$  Mev.

The  $\gamma$ -radiation emitted by the total calcium activity (including the long-lived positrons) consists of two components of which the energies are  $0.71 \pm 0.03$  Mev and  $1.4 \pm 0.1$  Mev. The energy of the softer  $\gamma$ -ray is quite close to the energy difference between the two groups of  $\beta$ -rays. We may therefore tentatively ascribe it to transitions between an excited state of  $\text{Sc}^{45}$  at 0.71 Mev above the ground state and the ground state. The two electron groups are thus due to  $\beta$ -decay of  $\text{Ca}^{45}$  to the excited and ground states, respectively. The 1.4 Mev  $\gamma$ -ray is probably due to  $\text{Na}^{22}$  contamination.

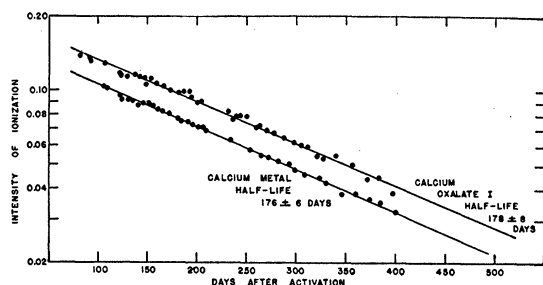
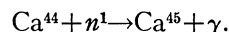
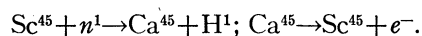


FIG. 3. Decay curves of  $\text{Ca}^{45}$  after activation with 8-Mev deuterons.

By subjecting spectroscopically pure calcium oxide to a prolonged bombardment with slow neutrons, evidence has been obtained for the formation of  $\text{Ca}^{45}$  according to the reaction



$\text{Ca}^{45}$  has also been chemically separated from high purity scandium oxide which had been bombarded inside a cadmium box with neutrons from a beryllium target which was bombarded for 700 microampere hours with deuterons of energy 8 Mev. One sample of active calcium carbonate was purified by redissolving and reprecipitating in the presence of inactive scandium on four separate occasions yet it retained the long period activity.  $\text{Ca}^{45}$  has therefore been produced by the reaction



No short-lived activity was obtained, proving that neither the 2.5-hour period nor the 30-minute period are associated with  $\text{Ca}^{45}$ .

Since  $\text{Ca}^{45}$  has such a long half-life and as it does not give rise to a radioactive product, it should be a useful tool in biological research for it appears probable that by using the probe method originated by Wilson and Kamen<sup>7</sup> strong samples of the active body may be produced. Unfortunately most of the emitted radiations are relatively soft and are readily absorbed. However, useful work has been done using  $\text{S}^{35}$  which emits even less penetrating electrons so that this difficulty can certainly be overcome.

#### BOMBARDMENT OF CALCIUM WITH FAST NEUTRONS

By bombarding calcium with fast neutrons, Pool, Cork and Thornton<sup>8</sup> observed a weak activity of half-life  $4.5 \pm 0.5$  min. which they ascribed to  $\text{Ca}^{39}$ . In similar experiments one of us (H.W.)<sup>9</sup> has previously separated from calcium two radioactive potassium isotopes with half-lives  $18 \pm 1$  min. and  $12.5 \pm 0.5$  hours, respectively, the latter being due to  $\text{K}^{42}$ .

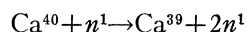
These experiments have been repeated several

<sup>7</sup> R. R. Wilson and M. D. Kamen, Phys. Rev. **54**, 1031 (1938).

<sup>8</sup> Pool, Cork and Thornton, Phys. Rev. **52**, 239 (1937).

<sup>9</sup> H. Walke, Phys. Rev. **52**, 663 (1937).

times, and the activity of half-life  $4.5 \pm 0.5$  min. has been observed even with very high purity calcium oxide. It seems likely, therefore, that it is a specific calcium effect and not due to impurity. However, the activity is so much weaker than the other fast neutron activities in calcium that it would seem rather unlikely that this is  $\text{Ca}^{39}$  due to the reaction



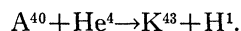
for  $\text{Ca}^{40}$  is 97 percent abundant compared with 0.6 percent for  $\text{Ca}^{42}$  from which  $\text{K}^{42}$  is produced.

Moreover, as has been pointed out by Professor Wigner,\* if one extrapolates the results of White, Delsasso, Fox and Creutz<sup>10</sup> for the half-lives of nuclei of the type  $(n-p) = \pm 1$ , it can be estimated that the half-life of  $\text{Ca}^{39}$  is probably less than one second and that the maximum energy of the emitted positrons should be about 4.9 Mev.

It has not yet been possible to separate the 4.5-min. body chemically. At the moment, therefore, we cannot identify it.

A search has been made for long-lived isotopes of potassium by bombarding calcium with fast neutrons for long periods, but none have been detected.

Moreover, the mass number of the potassium isotope of half-life  $18 \pm 1$  minutes has not been identified. If it were  $\text{K}^{43}$ , one might expect to observe the 18-minute period by bombarding argon with energetic  $\alpha$ -particles, the reaction being



Such an experiment has been performed by bombarding argon at atmospheric pressure with  $\alpha$ -particles of 16 Mev energy for 3 microampere hours but no induced radioactivity was detected.

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\* Private communication.

<sup>10</sup> White, Delsasso, Fox and Creutz, *Phys. Rev.* **56**, 512 (1939).

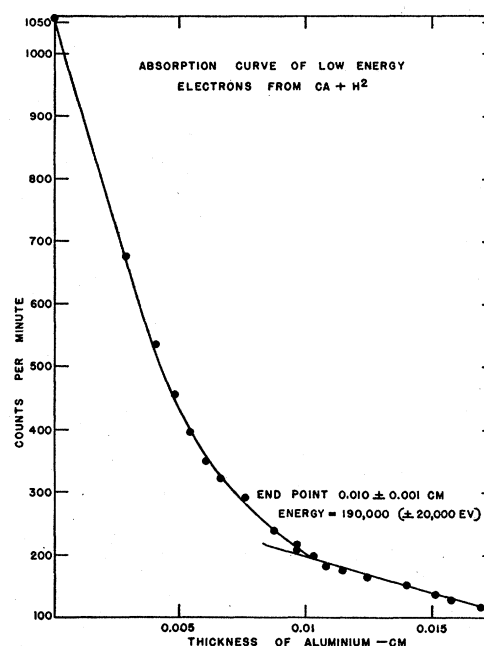


FIG. 4. Absorption in aluminum of low energy  $\beta$ -rays from  $\text{Ca}^{45}$ .

hospitality he has extended to one of us (H. W.) during his stay in Berkeley.

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#### APPENDIX

##### Chemical procedure used with calcium metal which had been bombarded with 8-Mev deuterons

The active layer was scraped off and dissolved in dilute HCl to which was added 50 mg of NaCl, 20 mg of  $\text{ScCl}_3$  and KCl, and excess of  $\text{NH}_4\text{Cl}$ . (The latter was included to prevent the precipitation of calcium as hydroxide during the separation of the scandium.) The scandium was then precipitated as  $\text{Sc}(\text{OH})_3$  by the addition of carbonate free ammonia. The  $\text{Sc}(\text{OH})_3$  was filtered off and after washing was redissolved in dilute HCl containing  $\text{CaCl}_2$ , NaCl and KCl and excess  $\text{NH}_4\text{Cl}$ .  $\text{Sc}(\text{OH})_3$  was then reprecipitated and the whole process repeated twice more. After three

purifications, the  $\text{Sc}(\text{OH})_3$  was dissolved in dilute  $\text{HCl}$ . Finally the solution was neutralized and the scandium precipitated as oxalate.

The filtrate from the first precipitation of  $\text{Sc}(\text{OH})_3$  was purified by adding traces of inactive  $\text{ScCl}_3$  and precipitating the scandium as hydroxide with  $\text{NH}_4\text{OH}$ .  $\text{Sc}(\text{OH})_3$  was removed three times in this manner, and it was assumed that the solution was thus freed of active scandium. Calcium was then extracted as follows: The solution was heated on a water bath and the calcium precipitated as oxalate by adding ammonium oxalate in excess. The calcium oxalate was filtered off and after washing was redissolved in  $\text{HCl}$ . Inactive  $\text{NaCl}$  and  $\text{KCl}$  were added to the solution which was then neutralized. The calcium was reprecipitated as oxalate, filtered and washed. It was assumed to be free of  $\text{Sc}$ ,  $\text{Na}$  and  $\text{K}$ .

The residual solution was heated and oxalate removed by adding inactive calcium chloride in excess. The insoluble calcium oxalate was removed and the solution thus purified

of calcium. Excess calcium was then carefully removed by adding small amounts of ammonium oxalate and filtering. After four such treatments, it was assumed that the solution was free of calcium.

After removing the calcium, the filtrate was evaporated to dryness to drive off  $\text{NH}_3$  and the residue was dissolved in water. From this potassium was precipitated as perchlorate by the addition of perchloric acid and ethyl alcohol.

The residual solution was finally acidified with concentrated  $\text{HNO}_3$  and the perchloric and nitric acids distilled off. The small residue containing the sodium was dissolved in water and evaporated to dryness.

It was found that the scandium and potassium precipitates were completely inactive as determined with a thin-walled counter. Most of the activity was found in the calcium oxalate which was observed to emit the soft electrons of  $\text{Ca}^{45}$  and  $\gamma$ -rays, but some activity remained in the sodium residue and could not be separated from it.

## Acceleration of Electrons in a Crystal Lattice

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The motion of an electron in a periodic potential field, and accelerated by a uniform field, can be obtained by treating the time-dependent Schroedinger equation. The result shows that the wave vector increases linearly with the time within the bounds of a single Brillouin zone. At the boundaries of the zones transitions to other zones may take place if the accelerating field is large enough.

THE motion of an electron in a periodic potential field has been studied extensively in connection with the theory of solid bodies. The energy characteristic functions are known to have the form

$$\psi_{\mathbf{k}}(\mathbf{r}, t) = u_{\mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) \exp[-iE_{\mathbf{k}}t/\hbar], \quad (1)$$

where  $\mathbf{k}$  is called the wave vector, and the function  $u_{\mathbf{k}}(\mathbf{r})$  is periodic in  $\mathbf{r}$  with the period of the potential energy. When no boundary conditions are imposed,  $\mathbf{k}$  can take on any value, and, except along certain surfaces which are boundaries of the Brillouin zones,  $u_{\mathbf{k}}$  and  $E_{\mathbf{k}}$  are continuous functions of  $\mathbf{k}$ . It is frequently convenient to use, instead of  $\mathbf{k}$ , the reduced wave vector. This differs from  $\mathbf{k}$  by a vector of the reciprocal lattice, and lies in the first Brillouin zone.

The motion of the electrons when a uniform

electric field is superimposed on the periodic field has presented a little difficulty, because of the fact that the potential of such a field becomes infinite, and the position of its zero value has no physical significance. If boundaries are put on the field there appear boundary effects that are believed to be of no significance in treating the behavior of electrons in crystals. If such boundaries are not used, the integrals involved diverge. Bloch<sup>1</sup> originally handled the problem by constructing a wave packet out of functions of the form (1). The motion of such a packet led to the conclusion that the wave vector  $\mathbf{k}$  changes at a uniform rate under the influence of an external field, but the method of proof was such as to be valid only when  $\mathbf{k}$  was far from the edge of a Brillouin zone. No indication was given of the

<sup>1</sup> F. Bloch, *Zeits. f. Physik* **52**, 555 (1928).