ARTIFICIAL ACTIVITY OF HAFNIUM AND SOME OTHER ELEMENTS

BY

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Artificial Radioactivity of Hafnium.

S ome time ago we found that under the action of neutron bombardment a radioactive isotope of hafnium is produced, the activity decaying with a period of a few months(4). To determine the period of decay more exactly, we activated 280 mgm. of hafnium oxide prepared by one of us(3) by placing it in a paraffin block together with radium-beryllium sources, containing 600 mgm. of radium element as sulphate and twenty times as much metallic beryllium powder. After irradiation for three months the hafnium oxide was removed from the paraffin block and put into an aluminium dish having a surface of 1.2 cm² and a height of 2 mm. The dish was placed directly below the aluminium window of our counter, the window having a thickness of about 20 μ. We followed the decay of the hafnium

Table 1.
Decay-measurement of Hafnium.

Date	Nr. of Days	Kicks/min.
17. VIII. 36.............	0	16.1
18. VIII. 36.............	1	15.3
24. VIII. 36.............	7	13.7
12. IX. 36.............	25	12.0
29. X. 36.............	73	7.8
7. I. 37.............	143	2.3
22. I. 37.............	158	1.8
25. II. 37.............	192	1.0

preparation for 200 days by comparing its activity with that of an uranium standard. The decay curve obtained is seen in fig. 1 and table 1.

From the latter we can conclude that the half life of hafnium is 55 ± 10 days (standard mean square deviation).
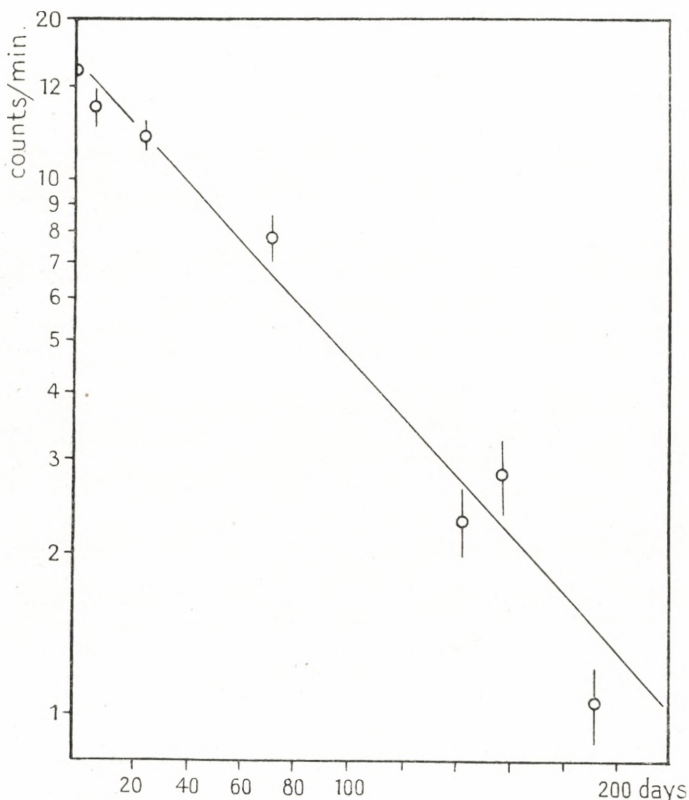

Fig. 1. Decay Curve of Hafnium.

Our initial activity was 20 kicks per min., the natural effect being about 4 kicks per min. We followed the decay curve until we had a net activity of 1 kick per min. From the fact that, in spite of the long activation, such a modest activity was obtained we can conclude that hafnium does

not belong to the elements showing a strong artificial radio-activity. This is partly due to the fact that the capture of neutrons by most of the hafnium isotopes leads, as explained later, to the formation of a heavier stable isotope; as stable isotopes 176, 177, 178, 179, and 180 are known and only the absorption of neutrons by the last mentioned isotope can lead to the formation of an avtive product. The relative abundance of the isotopes in the naturally occurring element hafnium, as determined by ASTON, is seen from table 2.

Table 2.
Relative Abundance of the Hafnium Isotopes.

Mass number	Abundance
176	5 %
177	19 %
178	28 %
179	18 %
180	30 %

We measured also the absorption in aluminium of the β-rays emitted by hafnium. The values obtained are seen from table 3.
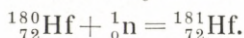
Table 3.
Absorption in Aluminium of the β-rays Emitted by Hafnium.

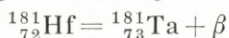| Thickness of the Al-foil	Kicks/min.
0	15.8
11 mgm./cm²	10.2
16.5 mgm/cm²	7.4

(half value thickness: 16 ± 1 mgm./cm²).

From the figures in table 3 follows that an aluminium layer of 16 mgm. per cm² reduces the intensity of the β-rays

emitted by a hafnium oxide layer of 230 mgm/cm² to one half
of its initial value. The comparison of the absorbing power
of aluminium for the β-rays of hafnium and scandium, de-
caying with periods of 55 and 90 days respectively, shows
no great difference; the ratio of the two half-value thick-
nesses being 1. 2. The softness of the hafnium radiation is
partly responsible for the low activities obtained after long
exposure of hafnium oxide with radium-beryllium sources of
a few hundred milliCurie, the β-radiation emitted being ab-
sorbed to an appreciable extent in the hafnium oxide sample
itself. In the case of hafnium, as already mentioned, every
place between the mass numbers 176 and 180 is occupied
by a known stable isotope; the formation of the active
hafnium isotope can, then, only be due to the process

$$^{180}_{72}\text{Hf} + ^{1}_{0}\text{n} = ^{181}_{72}\text{Hf}.$$

On emitting β-rays according to the equation

$$^{181}_{72}\text{Hf} = ^{181}_{73}\text{Ta} + \beta$$

the active hafnium isotope becomes the only stable isotope
of tantalum known. Hafnium is thus partly converted into
tantalum under the action of neutron bombardment, while,
as shown by us previously, hafnium is formed under the ac-
tion of neutrons on lutecium. It is quite possible that, under
bombardment with a powerful stream of deuterium or of
neutrons, further decay periods of hafnium will be discovered.

The Effect of Neutron Bombardment on Scandium.

A few years ago we embarked on the investigation of the
effect of neutron bombardment on scandium (4), (5), (6),
chiefly in the hope of being able to prepare an artificial radio-
active isotope of potassium and to get some information on
the then not entirely elucidated nature of the natural radio-
activity of potassium. We bombarded few grams of very

pure scandium oxide prepared by Prof. STERBA-BÖHM and used by Prof. HÖNIGSCHMIDT in his work on the atomic weight of scandium. After neutron bombardment the scandium oxide was dissolved in dilute hydrochloric acid and 100—150 mgm. of sodium chloride and the same amount of calcium oxide was added. The filtrate obtained after precipitation with carbonate-free ammonia was treated with oxalic acid and the calcium oxalate formed was removed. The sodium chloride which had been added to the solution of the scandium chloride compound was recovered after the removal of the ammonium chloride content of the last filtrate by evaporation. The activities of the three fractions, namely scandium oxide, sodium chloride, and calcium oxalate, were then determined. Only the two first preparations mentioned were found to be active. The activity of the scandium oxide decayed very slowly while the various sodium chloride fractions obtained in different experiments lost half of their slight activity within 10 and 18 hours. We had just finished the experiment mentioned when a note was published by FERMI and his collaborators(1) concerning the action of neutrons on potassium. They found that potassium captured neutrons by giving birth to a potassium isotope decaying with a half life of 16 hours. The values found by us for the period of the slight activity of different potassium preparations obtained from scandium showed a half life between 10 and 18 hours; we thought it justifiable, therefore, to identify the element found by us with that found by FERMI and his collaborators. The initial activities measured amounted usually to about 10 kicks/min. In one case, through the courtesy of the Medical Radium Station and Dr. J. C. JACOBSEN, we were loaned an unusually strong neutron source containing 600 milliCuries

radium-emanation. The decay curve obtained for potassium 42 in this experiment is seen from figure 2.

The activity found by us in the filtrate of scandium pre-cipitate could only be that of ^{42}K, as the presence of active impurities was excluded by the fact that the above mentioned
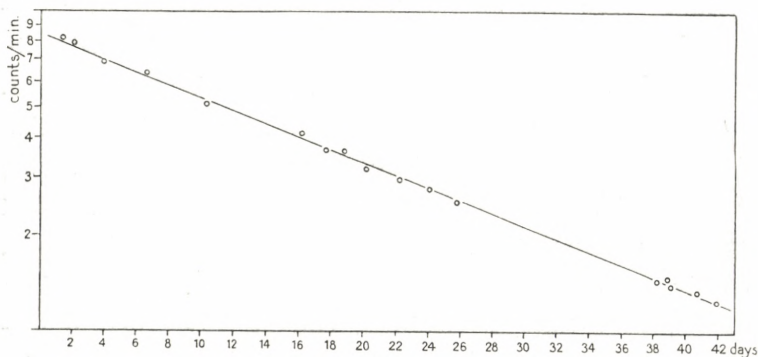

Fig. 2. Decay Curve of the Potassium Precipitate.

very pure scandium sample was used. The possibility that we measured the half life of radioactive sodium of 15 hours can be excluded with certainty not only for the reason mentioned above but also for the following reasons: So-dium, $^{24}_{11}$Na, can be prepared either from ^{23}Na by simple neutron capture, or from magnesium if the capture is followed by emission of a proton, or from aluminium if the capture is followed by emission of an α-particle. From the first mentioned process with the neutron sources at our disposal only very weak activities can be obtained even when starting with pure sodium. To prepare meas-urable amounts of radio-sodium from a few grams of impure scandium oxide an appreciable amount of magne-sium or aluminium would have had to be present in the preparation. 15 mgm. of aluminium mixed with 150 mgm. of ammonium nitrate, for example, gave after activation

to saturation less than o.5 kicks/min. and the activity obtained by similar amounts of magnesium with the same sources as used when activating scandium was still smaller. The amount of radio-sodium obtained from magnesium is less, and that of sodium by neutron capture very appreciably less than that obtained from aluminium. Scandium having just one stable isotope $^{45}_{21}$Sc, only the potassium isotope ^{42}K can be produced under neutron bombardment according to the equation

$$^{45}_{21}\text{Sc} + ^{1}_{0}\text{n} = ^{42}_{19}\text{K} + ^{4}_{2}\text{He}.$$
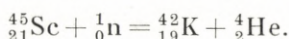
In the case of neutron capture by potassium, on the other hand, both reactions ^{39}K + n and ^{41}K + n can occur. While Fermi and his collaborators left it open which of the two last named potassium isotopes were produced, we could conclude from our experiments that the process witnessed by FERMI was ^{41}K + n = ^{42}K, and also that the process ^{39}K very probably leads to the formation of the potassium isotope ^{40}K which is responsible for the natural radioactivity of potassium. Recently WALKE(9), by making use of LAWRENCE's powerful cyclotron, which supplies a many thousand times stronger neutron beam as obtained from our radium-beryllium sources, was able to follow the decay of ^{42}K through ten periods and determined its half life period to be 12.4 ± 0.2 hours, i. e., a somewhat lower value than that following from our figure 2.

Besides preparing ^{42}K according to the equation

$$^{45}_{21}\text{Sc} + ^{1}_{0}\text{n} = ^{42}_{19}\text{K} + a.$$
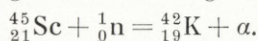
we succeeded(4) also in preparing this isotope by the process

$$^{42}_{20}\text{Ca} + ^{1}_{0}\text{n} = ^{42}_{19}\text{K} + ^{1}_{1}\text{H}.$$
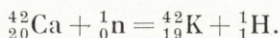
Walke(10), while reproducing FERMI's results and also ours as to the preparation of ^{42}K from scandium, was

unable to reproduce our experiments in which ^{42}K was prepared from calcium. This negative result induced us to repeate our experiments, this time by bombarding with fast neutrons as much as 1 kg of calcium carbonate. These were dissolved in a minimum amount of HCl, precipitated by a miminum amount of ammonium oxalate, which sufficed to precipitate all calcium after dissolving 100 mgm. of sodium chloride. Before we finished these experiments, a second paper of Walke(12),(13), was published in which he described successful experiments in producing ^{42}K from calcium, thus corroborating our statement.

Activity of Scandium.

After the removal of the radio-potassium produced, the scandium was still showing a weak activity which could not be removed by chemical operations and which we, therefore, had to ascribe to a radioactive isotope of scandium. The decay of the weak acitivity of scandium observed for 240 days is seen from table 4, which shows the presence

Table 4.
Activity of a Scandium Sample after Separation
of the Active Potassium.

Date	Nr. of Days	Kicks/min.
5. III. 36.	0	7.3 ± 0.6
21. III. 36.	16	6.0 ± 0.4
24. IV. 36.	50	7.2 ± 0.4
20. V. 36.	76	5.1 ± 0.4
5. VI. 36.	92	5.7 ± 0.4
1. VII. 36.	117	4.9 ± 0.3
13.VIII.36.	161	5.3 ± 0.4
24. X. 36.	233	4.4 ± 0.3

of a very weak activity decaying with a period longer than a year. We could not follow up this very weak activity further but concentrated our interest on another period ob-
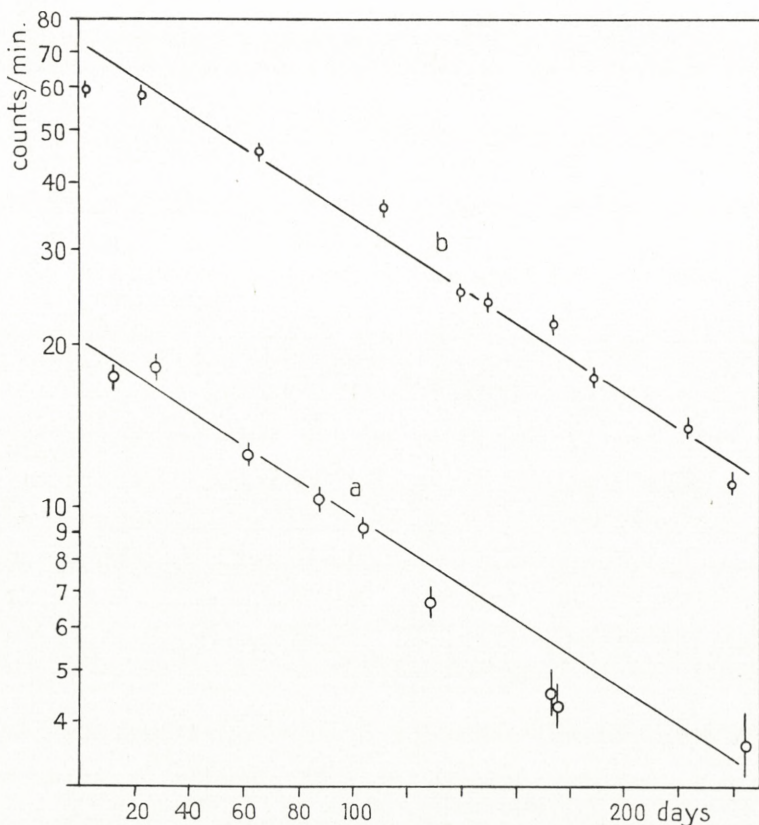

Fig. 3.   Decay Curve of Scandium Irradiated in a Paraffin Block for
a) 24 Days b) 50 Days.

tained after activating for 24 days in a paraffin block which contained emanation-beryllium sources of an average strength of 50 milliCuries. The result obtained is seen from figure 3a; the half life works out to be 90 ± 5 days.

In the next set of experiments we activated simultane-

ously three scandium preparations for 50 days with radium-
beryllium sources of a strength of about 200 milliCuries: one
in the usual way inside the paraffin block, the second one in
a paraffin block but with the preparation surrounded by
a shield of cadmium, which absorbed nearly 100 % of the
C-neutrons, and the third one with fast neutrons. The result
of the activation of the first named sample is seen from
figure 3b. The investigation of the second sample led to the
result that in the presence of cadmium the artificial radio-
activity of scandium is reduced to 2 % of the value obtained
in the absence of cadmium. From fig. 3b there follows for
the half life period of scandium the value 90 ± 5 days.
Quite recently Walke(13), by making use of Lawrence's
powerful cyclotron, bombarded scandium with deuterons
and obtained a period of 85 ± 2 days.

We want furthermore to mention an early experiment in
which we bombarded scandium with fast neutrons emitted
by a mixture of 600 milliCuries emanation and beryllium
powder; we observed a period of decay of about 50 hours.
As shown by Pool, Cork, and Thornton(8), and by
Walke(13), under bombardment with fast neutrons the
following two reactions occur as well:

$$^{45}_{21}Sc + ^{1}_{0}n = ^{43}_{21}Sc + 3\,^{1}_{0}n$$
$$^{45}_{21}Sc + ^{1}_{0}n = ^{44}_{21}Sc + 2\,^{1}_{0}n$$
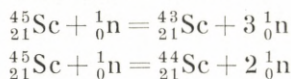
the scandium isotopes obtained emit positrons and have
half lives of 4 and 43 hours respectively; it was presumably
the last mentioned reaction which we observed.

Scandium 44 was also produced(13) by the action of
a-particles on potassium 41 and(11) by the action of
deuterons on calcium 43, while scandium 43 was produced
(11) by the action of a-particles on calcium 40, and(2)
by the action of deuterons on calcium 42.

WALKE was furthermore successful in producing scandium 42 under the action of α-particles on potassium 39, and of scandium 41 under the action of deuterons on calcium. The list of the known radioactive isotopes of scandium is therefore as follows from table 5.

Table 5.
Active Isotopes of Scandium.
(According to Walke(11)).

Active Isotope	Particle Emitted	Half life
^{41}Sc	positron	53 min.
^{42}Sc	positron	4.1 h
^{43}Sc	positron	4.0 h
^{44}Sc	positron	52 h
^{46}Sc	electron	85 days and possibly also a period of about 1 year.

We measured the reduction of counts when covering an active scandium preparation decaying with a period of 90 days with aluminium foils of varying thickness. The result obtained can be seen from table 6.

Table 6.
Absorption in Aluminium of the β-rays Emitted by Scandium.

Thickness of the Al-foil		Kicks/min.
1st experiment	0	12.5
	5.5 mgm./cm^2	8.8
	11.0 mgm./cm^2	7.1
2nd experiment	0	61.8
	11.0 mgm./cm^2	35.3
	16.5 mgm./cm^2	25.8

(half value thickness: 13 ± 1 mgm./cm^2)

In view of the softness of the β-rays emitted we used very thin scandium oxide layers; about 50 mgm./cm². In spite of the thin layers used the soft components were absorbed in the preparation to an appreciably greater extent than were the hard ones; accordingly we have to reckon with the possibility that the radiation emitted by scandium is still softer than indicated by the figures of table 6.

The Radioactivity of Europium and its Analytical Application.

In their fundamental research on the action of neutrons Fermi and his collaborators(1) investigated also the activity of a gadolinium preparation bombarded by neutrons and found an activity decaying with a period of 8 hours. A few years later, Sugden(7), investigating the radioactivity of europium, discovered a very strong avtivity decaying with a period of 9.2 h. and, at that time, interpreted the above mentioned period of decay of gadolinium to be due to the presence of some europium in the sample investigated. Investigations carried out by us, in which we made use of different gadolinium samples prepared by Prof. Rolla and partly by Prof. Prandtl and the late Baron Auer v. Welsbach, confermed completely the conclusion arrived at by Sugden, and this induced us to make use of the radioactivity of europium produced under the action of neutrons to determine the amount of europium present in gadolinium preparations. Prof. Rolla, being engaged in the preparation of large amounts of pure gadolinium compounds, sent us several samples the europium content of which he wished ascertained. We describe in the following the analytical procedure used by us.

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Thin layers of the gadolinium oxide samples to be investigated were fixed between two glass plates and placed within a paraffin block. Usually we investigated simultaneously the activation of 4 symmetrically placed preparations. It is of importance to bombard layers having the same thickness and to bombard them with neutrons in such a

Table 7.

Activity of Different Gadolinium Preparations. (The sample labelled „Standard" is the Gd_2O_3 to which 2 % Eu_2O_3 was added: samples 1—4 represent progressiv stages in the purification process carried out by Prof. Rolla).

Samples	kick/min.
"Standard"	125
1	60
2	60
3	30
4	25

way that each preparation is hit by the same number of neutrons; the latter was achieved by arranging the sources in the block circularly. We used in these experiments radium-beryllium sources containing 600 mgm. of radium, the neutron emission of which corresponds to that from about 400 milliCuries of radium emanation; in addition a beryllium-emanation mixture containing 300 milliCuries emanation was also present. After the lapse of 3 days an average mixture of each sample was placed in a small aluminium dish having a surface of 1.2 cm² and was put below the window of a Geiger-counter. The intensity of the activity of the different gadolinium samples investigated is proportional to the europium content. In order to arrive at a

figure stating the absolute concentration, we mixed 2 % of europium oxide with one gadolinium preparation denoted as sample 2 in table 7 and compared the activity of the latter with that of the gadolinium preparations of unknown europium content. The results are seen from table 7.

That, in spite of the large amount of radium and emanation used, the activities measured were not stronger is due to the high absorbing power of gadolinium, which reduces the density of thermal neutrons in the surroundings of the preparation. This effect is especially marked on account of the fact that the thermal neutrons diffuse and are likely to pass through the preparation several times. The latter effect can be best estimated by comparing the activity of pure europium oxide with that obtained when this material is embedded in gadolinium oxide. We activated simultaneously 200 mgm. of europium oxide and 200 mgm. of gadolinium oxide containing 2 % of europium. If gadolinium absorbed to the same extent as europium, the first named preparation should be 50 times more active than the last mentioned one. Actually we find the ratio to be 200 from which it follows that the presence of gadolinium in our preparations reduced the activity of europium to $1/4$ of the value which would have been obtained if the same amount of pure europium oxide had been subjected to the irradiation.

Summary.

The irradiation of hafnium with neutrons has been shown to produce a radioactivity with a half life of 55 ± 7 days and which may be ascribed to $^{181}_{72}\text{Hf}$. The intensity of the β-rays emitted is reduced to half of its initial value by an aluminium foil having a weight of 16 mgm./cm².

Scandium, $^{46}_{21}\text{Sc}$, was found to decay with a half life of 90 ± 5 days. The half value thickness for the absorption in aluminium of the β-rays from this element was found to be 13 mgm./cm².

The europium content of gadolinium oxide samples prepared by Professor LUIGI ROLLA was determined by making use of the artificial radioactivity produced under the action of neutrons on the europium present in the various samples.

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