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THE TRANSURANIUM ELEMENTS; EARLY HISTORY

Nobel Lecture given by

Edwin M. McMillan

at Stockholm on December 12, 1951

Berkeley, California

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In this talk I shall tell of the circumstances that led to the discovery of neptunium, the first element beyond uranium, and the partial identification of plutonium, the next one beyond that. The part of the story that lies before 1939 has already been recounted here in the Nobel lectures of Fermi and Hahn; I played no part in that and shall not repeat it now. Rather I shall start with the discovery of fission by Hahn and Strassmann. News of this momentous discovery reached Berkeley early in 1939. The staff of the Radiation Laboratory was put into a state of great excitement and several experiments of a nature designed to check and extend the announced results were started, using ionization chambers and pulse amplifiers, cloud chambers, chemical methods, and so forth.

I decided to do an experiment of a very simple kind. When a nucleus of uranium absorbs a neutron and fission takes place, the two resulting fragments fly apart with great violence, sufficient to propel them through air or other matter for some distance. This distance, called the "range," is a quantity of some interest, and I undertook to measure it by observing the depth of penetration of the fission fragments in a stack of thin aluminum foils. The fission fragments came from a thin layer of uranium oxide spread on a sheet of paper, and exposed to neutrons from a beryllium target bombarded by 8 Mev deuterons in the 37-inch cyclotron. The aluminum foils,

each with a thickness of about half a milligram per square centimeter, were stacked like the pages of a book in immediate contact with the layer of uranium oxide. After exposure to the neutrons, the sheets of aluminum were separated and examined for radioactivity by means of an ionization chamber. The fission fragments of course are radioactive atoms, and their activity is found where they stop.

The result of the experiment is shown in the first slide (Fig. 1). The horizontal scale indicates the depth in the stack of foils, in terms of equivalent centimeters of air. The vertical scale indicates the activities of the foils, measured about two hours after the end of the neutron bombardment. The greatest depth of penetration and therefore the maximum range of the fragments is seen to a little over two centimeters; the activity beyond this depth is that produced by the action of the neutrons on the aluminum itself, and it is seen to be nearly as great as the fission product activity on the first foil. There were however some interesting details of the fission process whose observation would be rendered difficult by this large background of activity. The fission fragments have various masses and therefore various ranges; is there any difference in the rate of decay of the long-range and short-range fragments? To find this out, I did a second experiment in which the foils were made of paper, a material which would not itself become radioactive. Since ordinary paper contains mineral matter, the backing for the uranium oxide was filter paper, and the thin foils were cigarette paper that had been extracted with acid. These were neither as thin nor as uniform as the aluminum foils, but that did not matter in this experiment.

Nothing very interesting about the fission fragments came out of this; the decay curves of the activities deposited on the various cigarette papers

were about alike. However, the filter paper, which held the uranium and at least half the fission products, showed something very interesting. Its decay curve was different; there was present a strong activity with a half-life of about 25 minutes, and another with a half-life of about two days. These lives could not be measured accurately because of the presence of part of the fission product activity in the same sample, but there was no doubt of their occurrence. The shorter period could with reasonable certainty be ascribed to the 23-minute uranium isotope U-239, discovered by Hahn, Meitner, and Strassmann in 1936. Since this is formed by simple neutron capture, it would not recoil out of the uranium oxide layer like the fission fragments. The two-day period could then be the product of the beta-decay of U-239, and therefore an isotope of element 93; in fact this was its most reasonable explanation. However, some time was to elapse before proof of this would be given.

The original purpose of the experiments just described was not very profound and the measurement of the range was not very precise, but the by-product, the two-day period, was very interesting. Therefore the technique was improved so as to increase the yield and purity of the non-recoiling activities. Sheets of bakelite were used as a backing, and a thin uniform layer of ammonium uranate was deposited on these by allowing it to settle out of a suspension. After activation, the layer of uranium compound was scraped off and its activity was studied. The next two slides show the decay curve of the first sample made in this way, a week after the note describing the earlier results had been submitted to the Physical Review. The first of these (Fig. 2) shows the later part of the decay curve, indicating the presence of a single substance with a 2.3 day half-life. On the same plot is the decay curve of a portion of the fission products caught

on a sheet of cellophane placed next to the uranium; it shows the continuous curvature characteristic of the mixed fission products. The second (Fig. 3) shows the early part of the decay curve. The black dots are obtained by subtracting the 2.3 day curve, and give a value of 23 minutes for the short periods, in exact agreement with the known period of U-239. The activity of the fission products caught on the cellophane is again shown.

When it thus became possible to prepare a new active substance in reasonably good purity by a simple physical means, the question of its chemistry could be investigated, and Segrè undertook to do this. The expected chemical properties of element 93, according to the periodic table, were those of rhenium. Segrè was very familiar with the chemistry of this element, since he and his co-workers had discovered another of its homologs, now called technetium, in 1937; this was the first of the synthetic elements to be found. He showed that the 2.3 day material had none of the properties of rhenium, and indeed acted like a rare earth instead. Since rare earths are prominent among the fission products, this discovery seemed at the time to end the story. However, as time went on and the fission process became better understood, I found it increasingly difficult to believe that one fission product should behave in a way so different from the rest, and early in 1940 I returned to the problem. By this time the 60-inch cyclotron was running and deuterons of 16 Mev were available. Two physical experiments were illuminating. In one, the effect of cadmium, which absorbs thermal neutrons was investigated. It reduced the fission product activity compared to the two non-recoiling activities, without changing the ratio of the latter. In the second, the earlier recoil experiments were repeated with a fission product catcher made of very thin collodion, and it was found that the range of the 2.3 day substance was

certainly not greater than 0.1 millimeters of air. These great differences in behavior from the fission products made the interpretation as a rare earth almost impossible.

At this point I started to do some chemistry, and in spite of what the Nobel committee may think, I am not a chemist. However, I did find that the 2.3 day period did not always follow the rare-earth chemistry consistently. For instance, in a fluoride precipitation with rare-earth carrier, sometimes only a part of the activity would come down, part remaining in solution. By now it was the Spring of 1940, and Dr. Philip Abelson came to Berkeley for a short vacation. He had been a graduate student in the Radiation Laboratory, working on the uranium activities, when fission was announced, and in fact the method he was using would inevitably have led to his discovery of that phenomenon. After getting his degree he had gone to the Carnegie Institution of Washington, and was there, unknown to me, trying to separate the 2.3 day period chemically from large samples of uranium on the basis of rare earth-like properties. When he arrived for his vacation and our mutual interest became known to one another, we decided to work together. I prepared the 2.3 day substance by the method described earlier, and he tried some new chemical ideas, finding the correct approach very quickly. The key to the situation was the state of oxidation of the material. When in a reduced state, it precipitates with rare earth fluorides; when in an oxidized state, it does not. In earlier work where the degree of oxidation was not controlled, erratic results are not surprising.

This suggests a strong similarity to uranium. The next slide (Fig. 4) illustrates some of the chemistry of uranium in water solution. The important valences are six and four; in the upper state it forms both positive and negative ions, uranyl and uranate, the transition between these being

governed by the acidity of the solution; in the lower state it is like thorium or 4-valent cerium. In hydrofluoric acid, uranyl fluoride is soluble while uranium tetrafluoride is insoluble, like the fluorides of the rare earths. Thus the results with element 93 would be explained if it had the same valence states with some of the same properties as uranium, differing in the stability of the two states, the lower state being relatively more stable in element 93. The similarity with uranium was further demonstrated by the following results. Four-valent uranium, like thorium and four-valent cerium, is precipitated by iodate, while the trivalent rare earths are not; element 93 in the reduced state came down with thorium iodate. Six-valent uranium forms a remarkable compound, sodium uranyl acetate, which can be precipitated from a strong sodium acetate solution; element 93 in the oxidized state came down with this precipitate, a reaction previously thought to be characteristic of uranium alone among all the elements.

When the chemistry of element 93 was known well enough to separate it from all other elements, Abelson and I were in a position to demonstrate its growth from the 20-minute U-239. This was done by taking a series of successive rare earth fluoride precipitates out of a chemically purified sample of the 23-minute uranium, in a reducing solution. The next slide (Fig. 5) shows the result. The initial activities of the samples, shown by the small circles, follow the 23-minute half-life of the parent substance, while each sample decays with a 2.3 day life, as indicated by the nearly horizontal lines at the right. With this proof of the genetic relation we could be sure that the 2.3 day substance was actually an isotope of element 93, which had escaped earlier identification only because its chemical properties are like those of its neighbor rather than those of its homolog.

A similar phenomenon of chemical similarity of neighbors occurs in the rare earths, and it was clear that this was happening again at element 93. The fact that some of the chemical properties of 4-valent 93 and 3-valent rare earths are alike is really only a coincidence; farther beyond uranium the elements actually become like the rare earths with a predominant 3-valent state, but of course Abelson and I did not know this at the time; when we spoke of a "second 'rare-earth' group of similar elements" in our note in the Physical Review, we were thinking only of the phenomenon of similarity of neighbors.

Before submitting that note we tried to identify the product of the decay of the 2.3 day substance, which we expected would be an alpha-emitter. We made a strong sample (11 millicuries) of the 2.3 day activity by chemical extraction from 500 grams of irradiated uranyl nitrate, and looked for alpha particle activity in this sample. This experiment was a failure, probably because our sample was too thick so that alpha-particles could not get out, and our published conclusion concerning the limiting value of the half life of the resulting alpha activity was the only serious error in our published note. (1)

After Abelson's rather industrious "vacation" was over I returned to the search for the alpha-particles. The lanthanum fluoride precipitate bearing the products of the decay of the strong element 93 sample did show an alpha activity, which was at first suspected of being due to contamination with natural uranium. However a measurement of the range showed that it was too long for that and therefore might actually be from the long-sought element 94. I then tried bombarding uranium directly with the 16-Mev deuterons from the cyclotron, in the hope that this might produce a different isotope of element 94 with a shorter life, giving a greater rate of alpha-particle

emission. This hope proved to be well founded, and a considerably stronger alpha-activity was found in the decay products of the element 93 separated from the deuteron-bombarded sample. The next slide (Fig. 6) shows the nuclear reactions involved in the formation of the two isotopes of element 94. At the time of which I am speaking, the half-lives of the alpha-emitters and the correct isotopic assignment of the one produced by deuterons were not known. However, the names "Neptunium" and "Plutonium" had already been suggested so it seems appropriate that the corresponding chemical symbols are shown on the slide. With these alpha-emitting samples I tried some chemical separations, finding that the alpha activity did not belong to an isotope of protactinium, uranium, or neptunium. It was precipitated along with four-valent cerium as the iodate, indicating a similarity to thorium and four-valent uranium. The natural supposition was that plutonium followed chemically the properties of uranium and neptunium, with the lower state still more stable than it is in neptunium. However I did not participate in the final proof of this, since I left Berkeley in November, 1940, to take part in the development of radar for national defense. The rest of the story belongs to Seaborg, who continued the work after my departure, and I shall let him tell it in his own way.

Notes

I have not given a list of references; such a list can be found in an excellent review of the subject:

The Trans-Uranium Elements,

by G. T. Seaborg and E. Segrè, Nature 159, 863 (1947).

(1) Another error in that note (reference 11 in Seaborg and Segrè) is in the value given for the upper limit of the beta energy of Np-239. The value printed (0.47 Mev) is a clerical or typographical error; the observed

end point of the absorption curve in aluminum was 250 milligrams per square centimeter, corresponding to an energy of 0.7 Mev. This is in agreement with later values obtained by the same method.

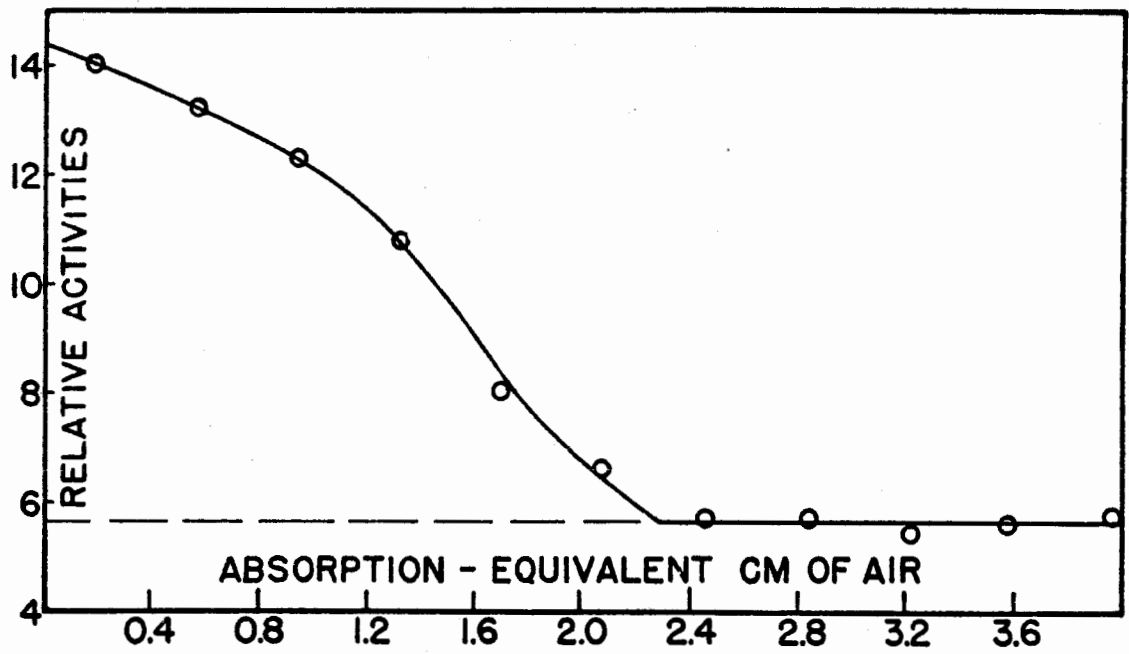
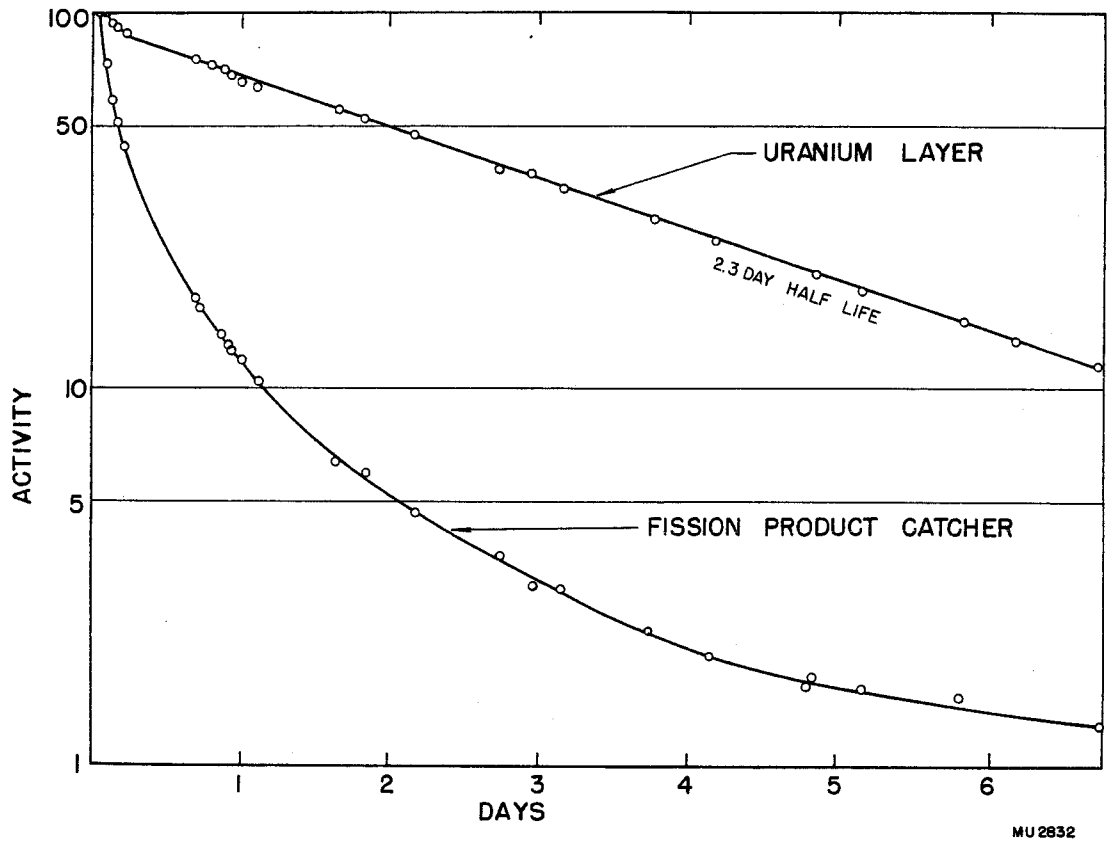
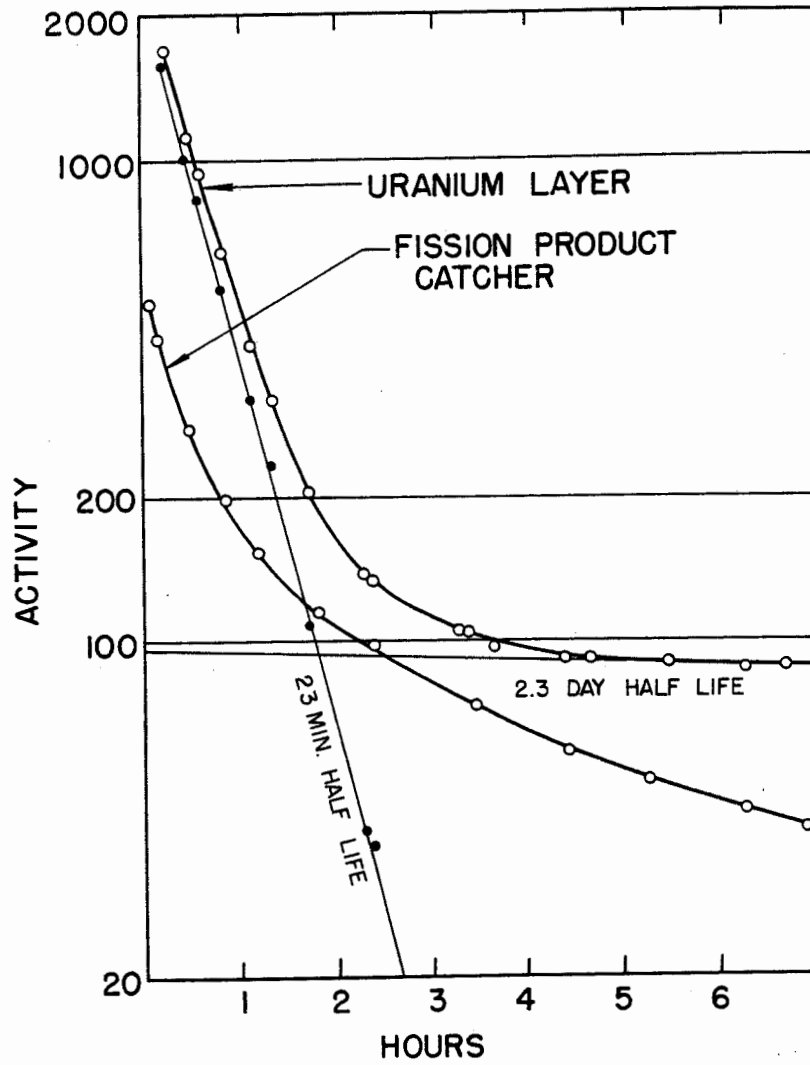


Fig. 1 Result of experiment to measure range of fission fragments.



MU 2832

Fig. 2 Later parts of decay curves of activity found in a thin layer of $(\text{NH}_4)_2\text{U}_2\text{O}_7$ after neutron irradiation, and in a piece of cellophane ("fission product catcher") that was next to the uranium layer during the irradiation.



MU 2833

Fig. 3 Early parts of same curves. The resolution of the "uranium layer" curve into 2.3 day and 23 minute periods is shown.

6 - VALENT URANIUM

ions: UO_2^{++} , UO_4^{--} , $\text{U}_2\text{O}_7^{--}$

compounds: UO_2F_2 is soluble.

$\text{Na}(\text{UO}_2)(\text{C}_2\text{H}_3\text{O}_2)_3$ is only slightly soluble.

4 - VALENT URANIUM

ion: U^{++++}

compounds: UF_4 is insoluble (like ThF_4 , LaF_3 , etc.)

$\text{U}(\text{IO}_3)_4$ is insoluble (like $\text{Th}(\text{IO}_3)_4$)

Fig. 4 Some pertinent chemical properties of uranium.

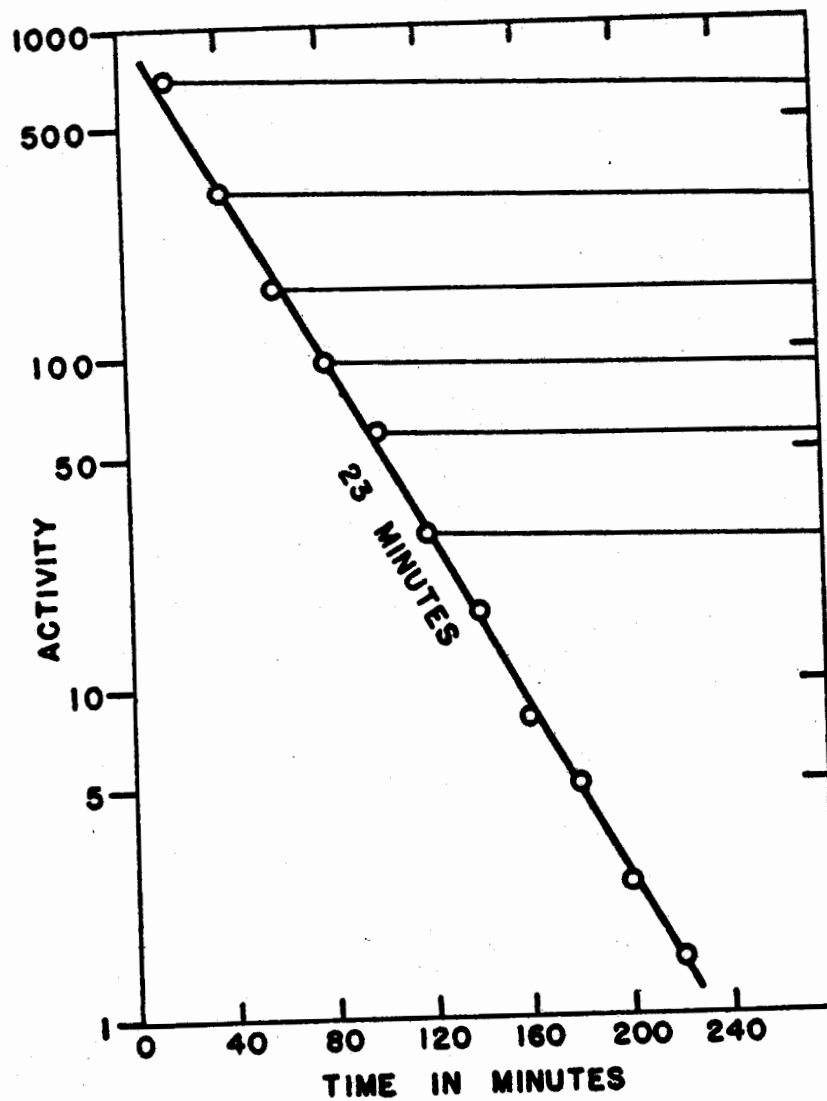
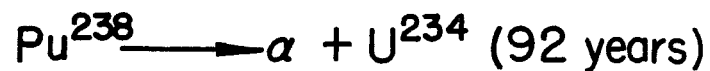
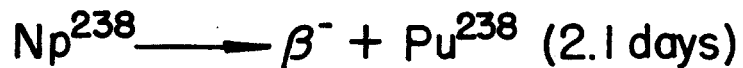
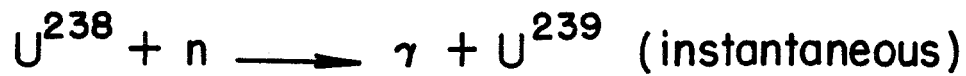


Fig. 5 Result of experiment to show the genetic relation between the 2.3 day and 23 minute substances.



MU 2834

Fig. 6 Nuclear reactions involved in the formation and decay of two plutonium isotopes. The figures at the right are the half-lives of the corresponding processes.