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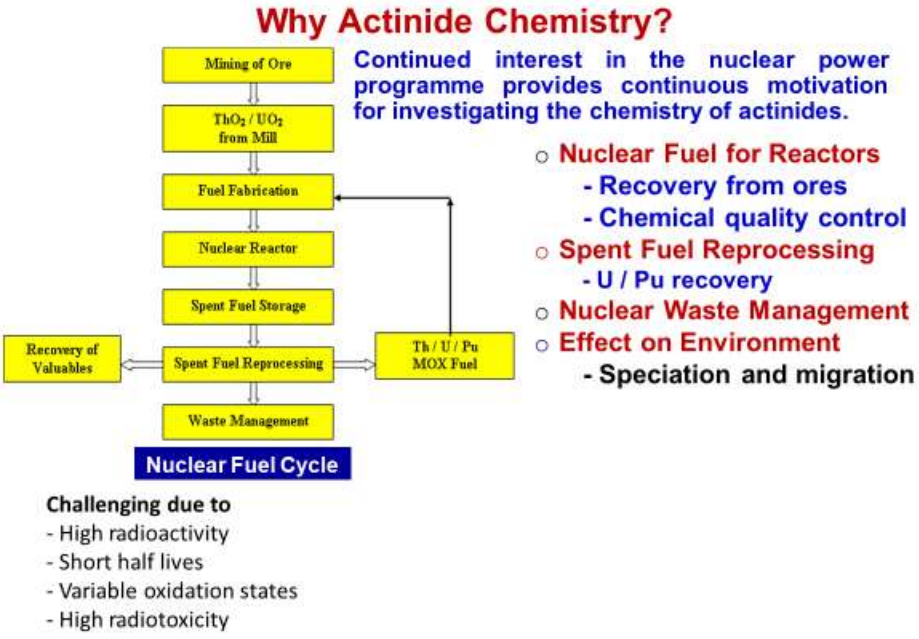
Week – 09
Lecture - 41

ACTINIDE CHEMISTRY

Introduction, Discovery and Synthesis of actinides

Hello, welcome to the lectures on the actinide chemistry. In this lecture series, we will be discussing about the actinides, their relevance and why one should be studying the chemistry of actinides. In this first lecture, I will be discussing the introduction, discovery and synthesis of actinide elements. The first question comes to our mind is why actinide elements? Because some of the early actinide elements like uranium and plutonium are having applications in the nuclear fuel cycle as the fuels. The fissile isotope of uranium and plutonium, that is 235 uranium and 239 plutonium can be used as the fuel material in the nuclear reactors. So that is why it is very, very important to study the chemistry of actinides.



So first I will give some example why this nuclear fuel cycle. Here, I have given a schematic of the nuclear fuel cycle where we start with the uranium ore. So that is how it starts with the mining of the uranium ore and this also involves the mining of the thorium ore because thorium can give the uranium-233, which we will be seeing in the course of this lecture series, that also is used in the AHWR reactors (as the fissile material). So, there it can be used as the fissile element.

Uranium-233 is used as the fissile element in the AHWR reactors. Therefore, thorium dioxide and uranium dioxide are obtained from the mining and milling operations. Then these elements and their compounds as the oxides, i.e., the oxides of thorium and uranium, in this case the uranium oxide is given for fuel fabrication. Some cases, if you need enriched uranium, then enrichment is also one of the steps before the fuel fabrication. Then after fuel fabrication it goes to the nuclear reactor and after the nuclear reactor is operated for a certain period of time, then the spent fuel where the fissile content has depleted significantly is removed from the nuclear reactor core and it is kept in a storage called the spent fuel storage where the radioactivity is decreased during the course of the time.

And afterwards the spent fuel reprocessing is done where the valuables like uranium and plutonium are recovered. In case of the AHWR fuel, we have to recover the thorium and also the uranium-233. And uranium and plutonium, they can be used as the mixed oxide fuel or the MOX fuel and again it goes back for fuel fabrication and to the reactor. So, this is the nuclear fuel cycle, also known as the closed nuclear fuel cycle, which

we will be discussing subsequently in this lecture. Now coming to the chemistry of actinides, it is very important because of its application in the nuclear reactors.

Also, after the nuclear reactor operation is over, the fuel is removed from the reactor core and then, as I mentioned, there is something called the spent fuel reprocessing. There also, the chemistry of actinide is important where the uranium and plutonium are recovered using a process called the PUREX process which we will be discussing subsequently in one of the lectures in greater detail. Then the raffinate which is coming out of the spent fuel reprocessing is taken out for the nuclear waste management program and there these actinides and the fissile products are vitrified and kept in the deep geological repositories. There also, the chemistry of actinide is important. Mostly the minor actinides like americium, curium and neptunium, their chemistry one needs to know such that this nuclear waste management can be carried out very efficiently.

Finally, there is also this effect of some of the hazardous actinides which are having large amount of radio toxicity. Their effect on the environment is also very important to know. That is why one needs to study the chemistry of actinides as well. In such cases, the speciation and migration of actinides, mainly that of plutonium, one needs to understand. Now apart from these applications, the nuclear fuel cycle and also this environmental chemistry of actinides is also a challenging study where this actinide chemistry one needs to study because of their very interesting and challenging chemistry.

Why it is challenging? Because of the high radioactivity of the actinides, their short half-lives. But also, one of the very important features of the actinide elements is their variable oxidation states and also very high radio toxicity. In view of this, the manipulations in the laboratory is very, challenging when one deals with the actinides. Now what are the actinides? We know them as the actinide elements and it appears that they are similar to the lanthanides. But about 80 years back when these man-made actinides were not discovered, it was not known which is the actinide series.

What are Actinides?

- The actinides or actinoids, as they are called, are f-block elements, where the electrons are filled in the 5f orbitals.
- The actinide series starts from Ac ($5f^0 6d^1 7s^2$) and ends with Lr ($5f^{14} 6d^1 7s^2$) and are considered to have similar physical and chemical properties.
- Though Ac does not have any f electron it is considered part of the series similar to La in the lanthanide series
- General electronic configuration of actinides: 2, 8, 18, 32, $5s^2$, $5p^6$, $5d^{10}$, $5f^{0-14}$, $6s^2$, $6p^6$, $6d^{0-2}$, $7s^2$ Or [Rn]
- Actinides give rise to decay series such as 4n (^{232}Th), 4n+1 (^{237}Np), 4n+2 (^{238}U) and 4n+3 (^{235}U)

And now we know that these actinides or actinoids as they are called are the f-block elements where the electrons are filled in the 5-f orbitals. The actinide series starts from actinium which have this electronic configuration of $5f^0$, $6d^1$ and $7s^2$ and ends with Lawrencium with the electronic configuration of $5f^{14}$, $6d^1$ and $7s^2$ and are considered to have similar physical and chemical properties. This is true mostly for the later part of the actinides as they have the similar chemical properties and physical properties. Though actinium does not have any f electrons, it is considered part of the series similar to lanthanum in the lanthanide series. General electronic configuration of the actinides given here, the outer core of radon is there and you have this filling of the electrons in the s, p, d and f cells as given here. The electronic configuration will be discussed separately in another lecture.

Actinides give rise to decay series such as the 4N which is thorium 232, 4N+1 that is actinium 237 series and 4N+2, 238 uranium and 4N+3 that is 235 uranium series which I am sure you have already studied in the schools. Now coming to whether these actinides are available in the nature. We know that these actinides like uranium, thorium are available in the nature in very large quantity and also, we know this actinium and protactinium also are available in the nature. What about the other actinides like plutonium? They were not available in the nature and they were synthesized around 1940 by Seaborg and his research group.

ACTINIDES IN NATURE: THE OKLO PHENOMENA

Interestingly, Pu is the highest atomic number element to occur in nature. Trace (ppt) quantities arise in natural uranium-238 deposits such as one in Oklo.

A natural nuclear fission reactor was suggested to have existed in Oklo, in Gabon, Africa as discovered by Francis Perrin in 1972. This is the only location where this phenomenon of self-sustaining nuclear fission reactions is known to have occurred. This is thought to have taken place approximately 1.7 billion years ago and probably continued for a few hundred thousand years.

--0.44 - 60% of ^{235}U was detected in the U of Oklo mines

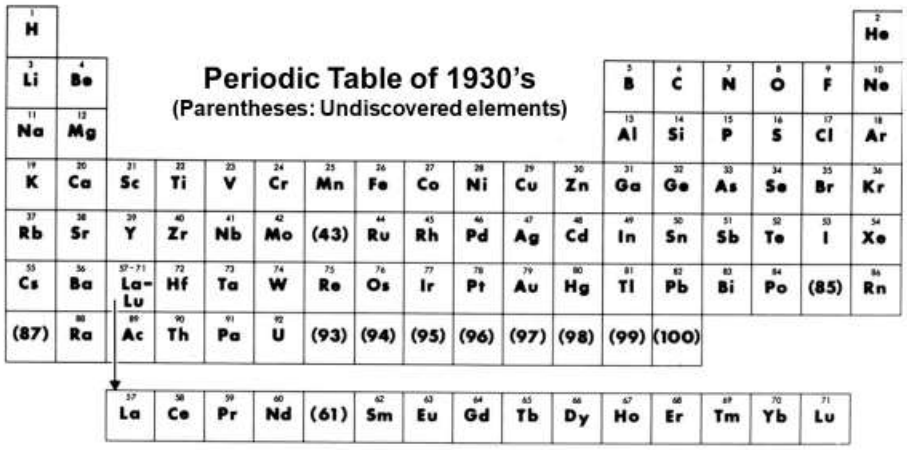
--Nd isotope monitoring was done for burn up measurement

--^{99}Ru fraction was more

--The reactor operated for several thousand years and stopped thereafter due to lower ^{235}U content and increased neutron poisons

--Reason for criticality: about 3.1% ^{235}U at that time

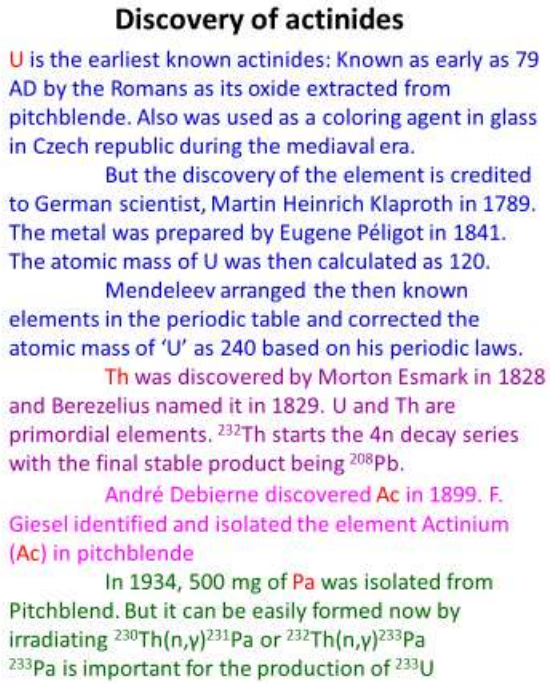
However, interestingly plutonium was detected in the nature and a trace quantity of plutonium was actually seen in the natural uranium (mainly U-238) deposits such as one in the Oklo, Gabon. This is called a natural fission reactor and was suggested to have existed in Oklo, Gabon, Africa. It was discovered by Francis Perrin in 1972 and this is the only location where this phenomenon of self-sustaining nuclear fission reaction is known to have occurred. This is thought to have taken place approximately 1.7 billions years ago and probably continued for a few thousands of years. Now why this was considered like this? This is because of the high amount of U-235 in that particular mine which is maybe more than whatever we are seeing, maybe around 3.1% of 235 Uranium was existing at that time. Now it is much less than that as you will be seeing in the subsequent slides. So, one thing is that relatively large fraction of 235 uranium was existing in the ores and secondly there are also signatures of this fission because the new Nd isotope monitoring was done from burn-up measurements and from the Nd isotopic ratio it was found out that definitely there is a change in this whatever expected from the normal U mines and from the Nd fission product isotopes, this signature was seen. Then ruthenium-99 fraction was more and also the reactor operated for several thousand years and stopped thereafter due to the lower U-235 content (due to the continuous fission reaction) and increased neutron poisons.



1913 Fajans and Goehring identified a short-lived isotope (^{234m}Pa) of protactinium (half-life 1.17 min.) while studying the ^{238}U decay

So, this suggested that plutonium was existing in this Oklo mines. Now coming to the periodic table, the actinides in the early part of the 20th century, were not placed in the periodic table the way we see them now. So, they were considered as similar to the transition elements. So, that we will be discussing subsequently and as you can see that only actinium, thorium, protactinium and uranium were discovered by that time. In 1913, Fazen and Goering identified a short-lived isotope of protactinium with a half-life of 1.17 minutes while studying the uranium-238 decay. So, this is how these actinides were discovered. First, we will see the discovery of actinides. That is the uranium is the earliest discovered actinide known as early as 79 AD by the Romans and its oxide extracted from pitchblende. It was also used as a coloring agent in glass in the Czech Republic during the

medieval era.

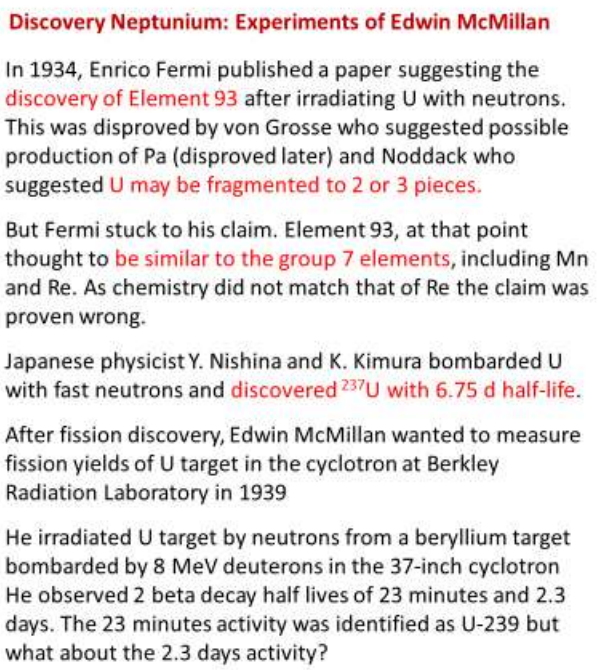


But the discovery of the element is credited to the German scientist Martin Heinrich Klaproth in 1789. The uranium metal was prepared by Eugene Peligot in 1841 and the atomic mass of uranium was then calculated as 120. Mendeleev arranged the then known elements in the periodic table and corrected the atomic mass of uranium as 240 based on its periodic laws. Coming to thorium, it was discovered by Morten Esmark in 1828 and Berzelius named it as Thorium in 1829. Uranium and thorium are primordial elements and Th-232 starts the 4N decay series as mentioned with the final stable product being ^{208}Pb.

Actinium was discovered in 1899 by Andre Debierne and F. Giesel identified and isolated the element actinium in pitchblende. In 1934, 500 milligrams of protactinium was isolated from pitchblende but it can be easily formed now by irradiating thorium 230 by an n gamma reaction giving 231-protactinium or irradiating thorium-232 by neutrons and the n gamma reaction giving 233- protactinium. The Pa-233 is an important isotope as it is decaying to U-233 which is the fissile element used in the AHWR reactors. Now the interesting thing is the discovery of neptunium.

Edwin McMillan is the first to have discovered neptunium in the Berkeley Radiation Laboratory in 1939. In 1934, however, Enrico Fermi has published a paper suggesting the discovery of element number 93 after irradiating uranium with neutrons. Fermi believed very strongly that he has discovered a different element because it was giving a lot of radioactivity. Now this was disproved by Van Grosse who suggested the possible production of protactinium which was disproved later on and Noddack who

suggested that uranium might have fragmented to two to three pieces of other radionuclides. This is of course before the nuclear fission was discovered. But Fermi stuck to his claim and he said that he has discovered element 93. At that point though, this was to be similar to the group 7 elements including manganese and rhenium. So, as uranium chemistry is similar to that of molybdenum and tungsten, similar way the element number 93 was believed to be similar to that of manganese and rhenium which are again transition elements. But the chemistry of the so-called element number 93 as claimed by Fermi didn't match to that of rhenium and that is how this claim was proven wrong. Subsequently, the Japanese physicists Nishina and Kimura, they bombarded uranium with fast neutrons around 1940 or so and they discovered uranium-237 with a half-life of 6.75 days. So, this discovery was correct, as we can see now, but the amount of uranium-237 which was isolated by them was too less because subsequently it was understood that uranium-237 decays to neptunium-237. But the neptunium-237 has a very long half-life and also this uranium-237 decayed to neptunium-237 which is 6.75 day half-life. So, the neptunium-237 which would have formed with a very, very less quantities that is how Nishina and Kimura they could not detect neptunium-237. Otherwise, they would have been the discoverer of this element.



However, after the discovery of fission, Edwin McMillan wanted to carry out some experiments to measure the fission yields of the uranium target in the cyclotron at the Berkeley radiation laboratory in 1939. So, he had carried out some experiments where he irradiated the uranium target by the neutrons coming from the beryllium target bombarded by the 8-MeV deuterons in the 37-inch cyclotron. So, he has used basically the thermal neutrons and he has seen that this uranium target which he has used which was a paper he

has taken on which he has sprayed the uranium metal compound. And there he was irradiating with neutrons and he found some radioactivity during the experiment which, he measured the profiles actually. He has taken several aluminum foils which are around 0.5 milligram per centimeter square thickness and he measured the activity as a function of the range. The aluminum foil he has subsequently dismantled and then measured as a function of the length (in the centimeter) or range in air. And he found this profile like this as given in the following figure (see the activity vs range plot). So, as the activity was seen decaying so this is attributed to the fission products and he found that there was a large amount of activity was still there. This is because of the aluminum foils.

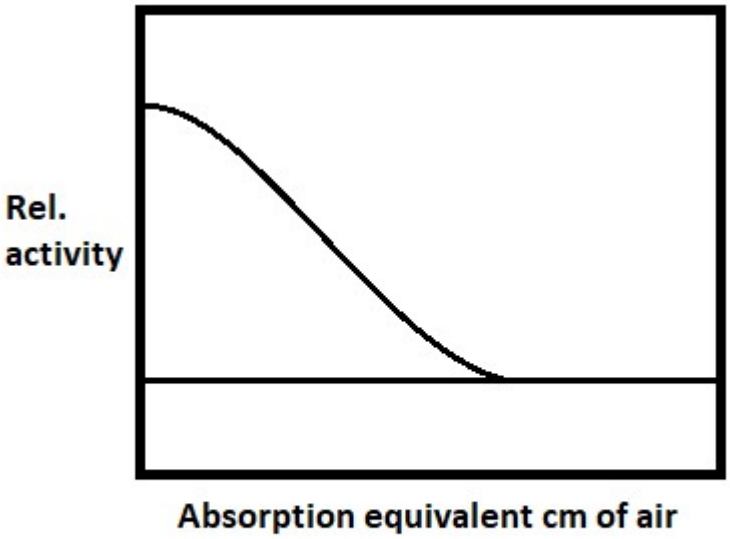


Fig. Results of experiments to get range of fission fragmants by McMillan

So, subsequently, he carried out some experiments where he had taken a paper actually instead of the aluminum he has taken paper and then he has stacked those papers and he found a very interesting trend. So he has plotted the activity as a function of hours and what he has seen is that there is a fission product catcher. These activities following this trend, this is a fission product catcher and there was a 23 minutes half-life pattern was seen and of course, there was another decay profile with 2.3 days half-life. So, basically he has seen the signature of 23 minutes half-life one radionuclide and 2.3 days half-life as another radionuclide. So, this was rather intriguing so he thought that there is definitely some new element that has formed but he wanted to prove it. How to prove it? So, he carried out subsequently a chemistry experiment and this will be the next slide. So, this chemistry experiment was carried out by Emilio Segre who is the discoverer of technetium and Segre was an expert in the chemistry of rhenium. So, when Macmillan approached Segre so he carried out the chemistry of rhenium for this isolated radioactivity.

Discovery Neptunium: Chemistry studies of Edwin McMillan and Philip H. Abelson (1940)

McMillan carried out chemistry along with **Emilio Segrè** to prove that the chemistry was similar to Re but with no success. When reacted with HF in oxidizing conditions it behaved like rare earths concluding it as a fission products

McMillan then collaborated with **Phil Abelson** and reacted with HF under reducing conditions leading to precipitation (like Th) suggesting it is not a rare earth element and in oxidizing conditions it precipitated by NaAc more like U

Finally, he concluded that the 23 minutes radionuclide is U-239 and the 2.3 d one is a new element akin to U and he named it as Neptunium

$^{238}U + n \rightarrow {}^{239}U \rightarrow {}^{239}Np$

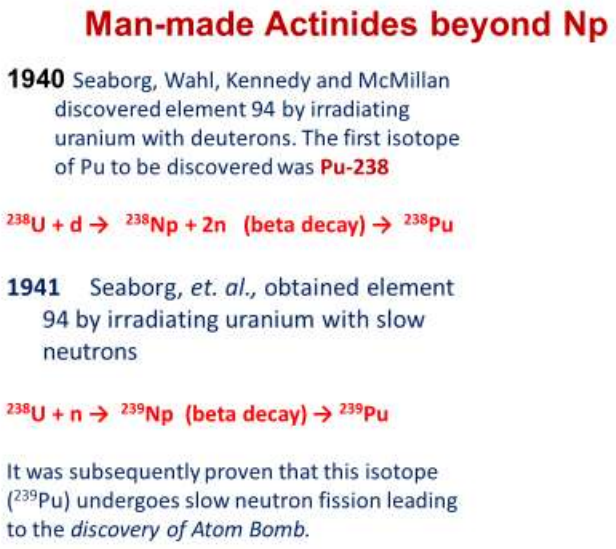
$^{235}U + n \rightarrow {}^{236}U + n \rightarrow {}^{237}U \rightarrow {}^{237}Np$

$^{238}U + n\ (fast) \rightarrow {}^{237}U + n$

What he did is he reacted with hydrofluoric acid in oxidizing conditions and it behaved like a rare earth concluding that it is a fission product and not a new element. So, that is how Macmillan thought that probably whatever he had discovered it may be a fission product but not a new element. However, after some time he collaborated with Phil Abelson and the same experiment was carried out instead of oxidizing conditions in reducing conditions and what he observed that there was a precipitation of this new element was possible similar to that of thorium. So, that is how he suggested that it is not a rare earth element and it is probably a different element. So, then what he did he repeated the experiment in oxidizing conditions and precipitated by sodium acetate.

So, then he concluded that it may be similar to that of uranium. So, finally Macmillan concluded that the 23 minutes radionuclide is nothing but uranium-239 which is actually neutron activated product of uranium-238 which is present in the natural uranium and the 2.3 days half-life radioactivity is nothing but a new element which is similar to that of Uranium and he named it as neptunium. So, the reaction which is giving neptunium-239 that is 238-uranium captures the neutron giving 239 uranium which undergoes beta decay giving Np-239. $^{238}U + n \dashrightarrow {}^{239}U \dashrightarrow {}^{239}Np$. Subsequently, the isotope ^{237}Np was discovered but in that case the reaction can be twofold it can be carried out by ^{235}U which

captures a slow neutron giving ^{236}U and which again captures another neutron giving ^{237}U which undergoes beta decay to give ^{237}Np.



Another reaction is ^{238}U can react with fast neutrons giving ^{237}U plus 1 neutron then this ^{237}U uranium again undergoes beta decay giving ^{237}Np.

$^{235}U + n \text{ --> } ^{236}U + n \text{ --> } ^{237}U \text{ --> } ^{237}Np$

$^{238}U + \text{fast n} \text{ --> } ^{237}U + 2n \text{ --> } ^{237}Np$

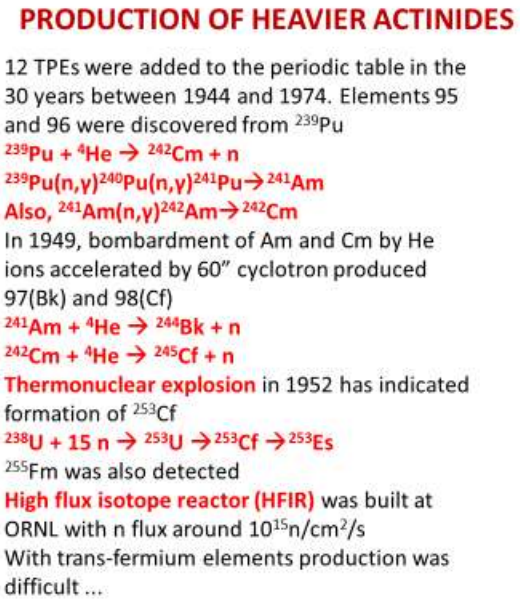
So, this is how neptunium was discovered. Now beyond neptunium subsequently many other actinides were discovered. ^{238}Pu was discovered by Seaborg, Wahl, Kennedy and McMillan in 1940 and this was called as element 94 where the uranium was irradiated by deuterons from this cyclotron facility as the Lawrence radiation laboratory and this was the first plutonium isotope which was discovered.

$^{238}U + d \rightarrow \ ^{238}Np + 2n \ \ (\text{beta decay}) \rightarrow \ ^{238}Pu$

Subsequently, of course ^{239}Pu was discovered by Seaborg et al. again by irradiating uranium-238 with slow neutron and this is the reaction.

$^{238}U + n \rightarrow \ ^{239}Np \ \ (\text{beta decay}) \rightarrow \ ^{239}Pu$

Uranium 238 which captures the neutron giving ^{239}Np as already we have seen and it undergoes beta decay giving ^{239}Pu. So, this ^{239}Pu is very important as it is a fissile isotope of plutonium and it is used in our reactor and subsequently it was used in the atom bomb.



Now the production of heavier actinides. Between 1944 and 1974, 12 trans-plutonium elements were added to the periodic table and element 95 and 96 were discovered that is the americium and curium as we know today. They were discovered from the ^{239}Pu plutonium so the reactions are given here.

$^{239}Pu + {}^{4}He \rightarrow {}^{242}Cm + n$

$^{239}Pu + n \rightarrow {}^{240}Pu + n \rightarrow {}^{241}Pu \rightarrow {}^{241}Am$

Plutonium-239 when it is undergoing a nuclear reaction with helium-4 gives ^{242}Cm plus neutron. Plutonium-239 can also undergo neutron capture reaction giving ^{240}Pu which again captures another neutron to give ^{241}Pu which again undergoes beta decay to give ^{241}Am. This ^{241}Am can also capture one neutron as given here to produce ^{242}Am and this can undergo beta decay to give ^{242}Cm.

$^{241}Am + n \rightarrow {}^{242}Am \rightarrow {}^{242}Cm$

So, this is how this curium and americium were discovered by Seaborg and his colleagues and subsequently in 1949 the bombardment of americium and curium by helium ions accelerated by the 60 inch cyclotron it produced element number 97 which is known as berkelium today and element number 98 which is known as californium. The reactions are given here where Am-241 reacts with He-4 to give ^{244}Bk and ^{242}Cm reacts with helium-4 to give ^{245}Cf.

$^{241}Am + {}^{4}He \rightarrow {}^{244}Bk + n$

$^{242}Cm + {}^{4}He \rightarrow {}^{245}Cf + n$

Subsequently, in 1952 the thermonuclear explosion was carried out and it has indicated the formation of ^{253}Cf.

You see from here that a large number of neutrons are captured by uranium-238 to give uranium-253 which decays to californium-253 and this californium-253 subsequently decays to Einsteinium-253. ^{255}Fm also was detected in this thermonuclear explosion and subsequently at ORNL this high flux isotope reactor that is HFIR was built with a neutron flux around $1x10^{15}$ neutrons per centimeter square per second. Lot of this heavier actinides were synthesized using this high flux isotope reactor and the trans-Fermium elements however were not possible and they were subsequently carried out by some nuclear reactions with some sort of fusion reactions were carried out which we will be discussing subsequently. Now these are the isotopes of the actinide elements as shown here from atomic number 89 to 103. As we see here 89 is actinium which was of course known before the synthetic actinide elements were produced in 1940.

ISOTOPES OF ACTINIDE ELEMENTS

At. No	Element	No of isotopes (range)		Natural abundance (%)
89	Actinium	33	204-236	NA, transient
90	Thorium	32	207-238	232(100)
91	Protactinium	30	211-240	NA, transient
92	Uranium	27	214-219,221-240,242	234(0.0055),235(0.72),238(99.27)
93	Neptunium	25	219,220,222-244	NA
94	Plutonium	20	228-247	NA
95	Americium	19	223,229,230,232-247	NA
96	Curium	19	233-251	NA
97	Berkelium	19	233,234,236,238-253	NA
98	Californium	20	237-256	NA
99	Einsteinium	18	240-257	NA
100	Fermium	20	241-260	NA
101	Mendelevium	17	244-260	NA
102	Nobelium	13	249-260, 262	NA
103	Lawrencium	16	251-266	NA

So, thorium, protactinium and uranium were known and from neptunium onwards as I have mentioned, these are man-made actinides and this number of isotopes written here see there are nearly 33 isotopes of actinium starting from 204 actinium to 236 actinium and mostly these are transient they are not very stable isotopes. For Th, there are 32 isotopes starting from ^{207}Th to ^{238}Th and the naturally occurring isotope of course is ^{232}Th which is 100% abundance. Protactinium has 30 isotopes starting from ^{211}Pa to ^{240}Pa and many of these are transient. For Uranium there are 27 isotopes starting from ^{214}U to ^{219}U then from

^{221}U to ^{240}U and ^{242}U. Out of these the naturally occurring isotopes are ^{234}U, ^{235}U and ^{238}U with the abundances of 0.0055%, 0.72% and 99.27%, respectively. Now all these heavier actinides starting from neptunium they are man-made. Similarly, for the man-made actinide elements the number of isotopes are listed in this table. Thank you.

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