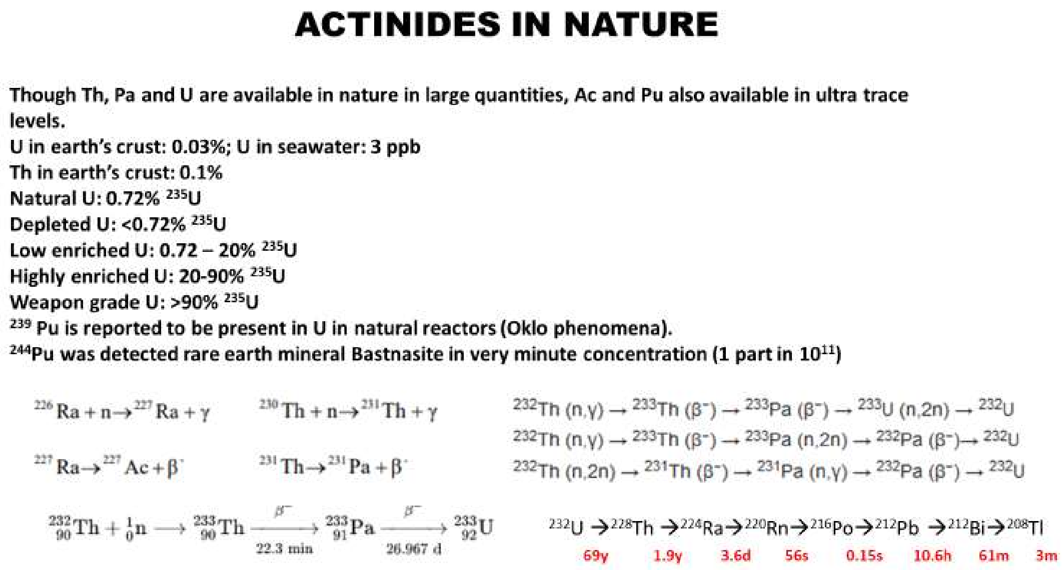
Course Name: Nuclear and Radiochemistry
Professor Name: Prof. P. K. Mohapatra
Department Name: Radiochemistry Division
Institute Name: Homi Bhabha National Institute
Week – 09
Lecture - 42



ACTINIDES IN NATURE

Though Th, Pa and U are available in nature in large quantities, Ac and Pu also available in ultra trace levels.
U in earth's crust: 0.03%; U in seawater: 3 ppb
Th in earth's crust: 0.1%
Natural U: 0.72% ^{235}U
Depleted U: <0.72% ^{235}U
Low enriched U: 0.72 – 20% ^{235}U
Highly enriched U: 20-90% ^{235}U
Weapon grade U: >90% ^{235}U
^{239} Pu is reported to be present in U in natural reactors (Oklo phenomena).
^{244}Pu was detected rare earth mineral Bastnasite in very minute concentration (1 part in 10^{11})

$^{226}Ra + n \rightarrow ^{227}Ra + \gamma$

$^{227}Ra \rightarrow ^{227}Ac + \beta^-$

$^{230}Th + n \rightarrow ^{231}Th + \gamma$

$^{231}Th \rightarrow ^{231}Pa + \beta^-$

$^{232}Th\ (n,\gamma) \rightarrow ^{233}Th\ (\beta^-) \rightarrow ^{233}Pa\ (\beta^-) \rightarrow ^{233}U\ (n,2n) \rightarrow ^{232}U$

$^{232}Th\ (n,\gamma) \rightarrow ^{233}Th\ (\beta^-) \rightarrow ^{233}Pa\ (n,2n) \rightarrow ^{232}Pa\ (\beta^-) \rightarrow ^{232}U$

$^{232}Th\ (n,2n) \rightarrow ^{231}Th\ (\beta^-) \rightarrow ^{231}Pa\ (n,\gamma) \rightarrow ^{232}Pa\ (\beta^-) \rightarrow ^{232}U$

$$^{232}_{90}Th + ^{1}_{0}n \longrightarrow ^{233}_{90}Th \xrightarrow[22.3\ \text{min}]{\beta^-} ^{233}_{91}Pa \xrightarrow[26.967\ \text{d}]{\beta^-} ^{233}_{92}U$$

$$\underset{69y}{^{232}U} \rightarrow \underset{1.9y}{^{228}Th} \rightarrow \underset{3.6d}{^{224}Ra} \rightarrow \underset{56s}{^{220}Rn} \rightarrow \underset{0.15s}{^{216}Po} \rightarrow \underset{10.6h}{^{212}Pb} \rightarrow \underset{61m}{^{212}Bi} \rightarrow \underset{3m}{^{208}Tl}$$

Welcome to the second lecture on actinides. In the previous lecture, we have discussed about the actinides and why it is important to study the chemistry of actinides and also some of the man-made actinides. I had given a detailed account of neptunium and plutonium synthesis. Now in this lecture, we talk about some of the other aspects like actinides in nature. So, though thorium, protactinium and uranium are available in the nature in large quantities, some of the other actinides which are also available in nature in very (very) trace levels are actinium and plutonium. It is surprising that plutonium also is available in ultra-trace levels as discussed in the previous lecture.

This plutonium comes as a consequence of the fission reactions taking place in nature wherein the very large deposits of uranium is there in the uranium mines like the Oklo phenomena at the Uranium mine in Oklo, Gabon, Africa. Now, in that mine, as I have already discussed, the fissile content of the uranium (^{235}U) was very high. In the earth's crust, at this moment we have around 0.03% uranium, the average value I have given here and in sea water, uranium is 3 ppb, very very low concentration of uranium. Nevertheless, it is a rich source of uranium if somebody can really tap uranium from the sea water. Now compared to uranium, thorium concentration is much higher in the earth crust. So, thorium in earth crust is around 0.1%. But in the sea water, thorium content is very less. It is probably because of the hydrolysis of thorium which is existing in the tetra valent oxidation state. Now coming to the natural uranium, we have the fissile content, i.e., ^{235}U as 0.72% and other uranium sources also can be defined here as:

-Depleted uranium: where the fissile content is <0.72% ^{235}U

-low enriched uranium: 0.72% to 20% ^{235}U

-Highly enriched uranium: 20% to 90% ^{235}U

-Weapon grade uranium: >90% ^{235}U

As I have mentioned, the ^{239}Pu which at ultra-terrace level is reported in this uranium natural reactors that is the OKLO phenomena where the ^{235}U content at that stage when this reactor was suggested to be operative was more than 3% 235U in the natural uranium in the mine at OKLO.

Now ^{244}Pu was detected in the rare earth mineral Bastnasite at very very minute concentration that is one part in 10^{11}. Now some of these other actinides like protactinium-231, can be formed by some of the reactions as is written here.

$^{230}\mathrm{Th} + \mathrm{n} \dashrightarrow {}^{231}\mathrm{Th} \dashrightarrow {}^{231}\mathrm{Pa}$

Similarly, ^{226}Ra which with a subsequent neutron capture gives ^{227}Ra, and the ^{227}Ra can decay to ^{227}Ac. So, this is how ^{227}Ac is formed and the ^{231}Pa formed from thorium-230 which by neutron capture to give 231-thorium and then 231-thorium decays by beta decay to ^{231}Pa. So, this is how protactinium is formed and also actinium is formed, i.e., ^{227}Ac. Another isotope of protactinium which is very important is ^{233}Pa. It is obtained by irradiating ^{232}Th by neutrons and you get ^{233}Th which has a 22.3 minutes half-life and by beta decay it gives ^{233}Pa protactinium which undergoes another beta decay to give ^{233}U.

$^{232}\mathrm{Th} + \mathrm{n} \dashrightarrow {}^{233}\mathrm{Th} \dashrightarrow {}^{233}\mathrm{Pa}$

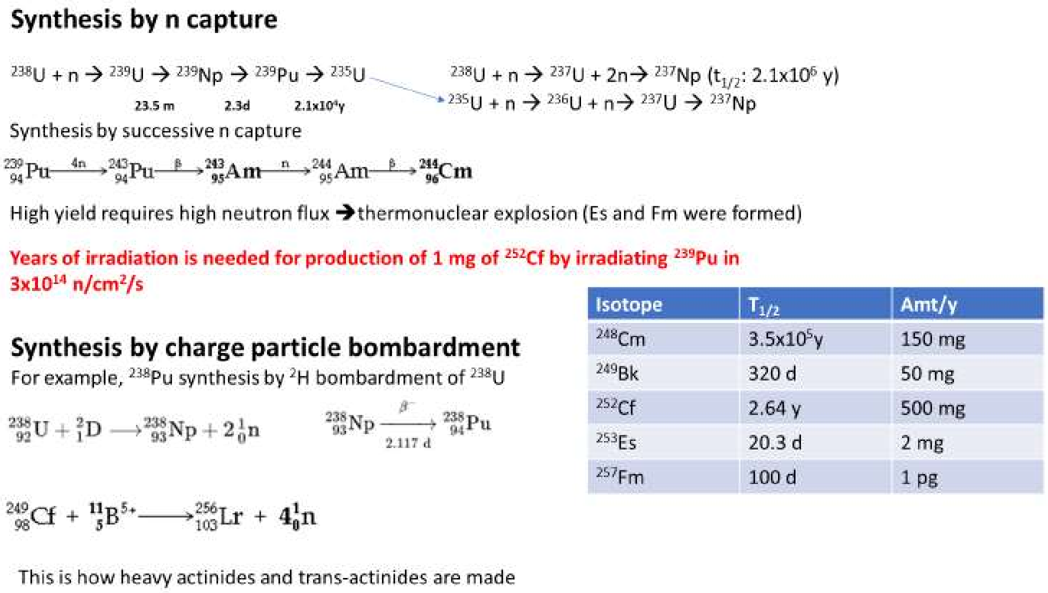
^{233}U is very important again for reactors which are operating on ^{233}U as the fissile material, i.e., the AHWR. Now when this reaction is taking place there is also the possibility of uranium-232 formation which is formed by different reactions as given here like from ^{232}Th thorium it can form ^{233}Pa which by beta decay goes to uranium-233 as I have already mentioned but this ^{233}U can also undergo a n,2n reaction to give ^{232}U.

$^{232}\mathrm{Th} + \mathrm{n} \dashrightarrow {}^{233}\mathrm{Th} \dashrightarrow {}^{233}\mathrm{Pa} \dashrightarrow {}^{233}\mathrm{U} + \mathrm{n} \dashrightarrow {}^{232}\mathrm{U} + 2\mathrm{n}$

Alternatively, the protactinium-233 in the same reaction before decaying to ^{233}U it can also undergo (n,2n) reaction to give ^{232}U.

$^{233}\mathrm{Pa} + \mathrm{n} \dashrightarrow {}^{232}\mathrm{Pa}\ (+\ 2\mathrm{n}) \dashrightarrow {}^{232}\mathrm{U}$

Thorium-232 also can undergo (n,2n) reaction to give ^{231}Th which by beta decay gives protactinium-231 and which can capture a neutron and by n,ϒ reaction it goes to ^{232}Pa which undergoes beta decay to give the ^{232}U. So, this is how actually this uranium-232 is formed in a rather small quantity while producing ^{233}U but it is very important because this ^{232}U has to be removed from the ^{233}U otherwise the operation becomes very difficult as you can see from this decay reaction shown here from uranium-232 which goes to ^{228}Th and then to ^{224}Ra radium and to ^{220}Rn which then decays to ^{216}Po followed by to ^{212}Pb lead and these are all by alpha decay and then ^{212}Pb undergoes beta decay to form ^{212}Bi which undergoes another alpha decay to give ^{208}Tl which is a hard gamma emitter and this gives significant dose to the working personnel.



Synthesis by n capture

$^{238}U + n \rightarrow {}^{239}U \rightarrow {}^{239}Np \rightarrow {}^{239}Pu \rightarrow {}^{235}U$

23.5 m 2.3d 2.1x10^{4}y

$^{238}U + n \rightarrow {}^{237}U + 2n \rightarrow {}^{237}Np$ ($t_{1/2}$: 2.1x10^{6} y)

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

Synthesis by successive n capture

$${}^{239}_{94}Pu \xrightarrow{4n} {}^{243}_{94}Pu \xrightarrow{\beta} {}^{243}_{95}Am \xrightarrow{n} {}^{244}_{95}Am \xrightarrow{\beta} {}^{244}_{96}Cm$$

High yield requires high neutron flux ➔thermonuclear explosion (Es and Fm were formed)

Years of irradiation is needed for production of 1 mg of ^{252}Cf by irradiating ^{239}Pu in 3x10^{14} n/cm^{2}/s

Synthesis by charge particle bombardment

For example, ^{238}Pu synthesis by ^{2}H bombardment of ^{238}U

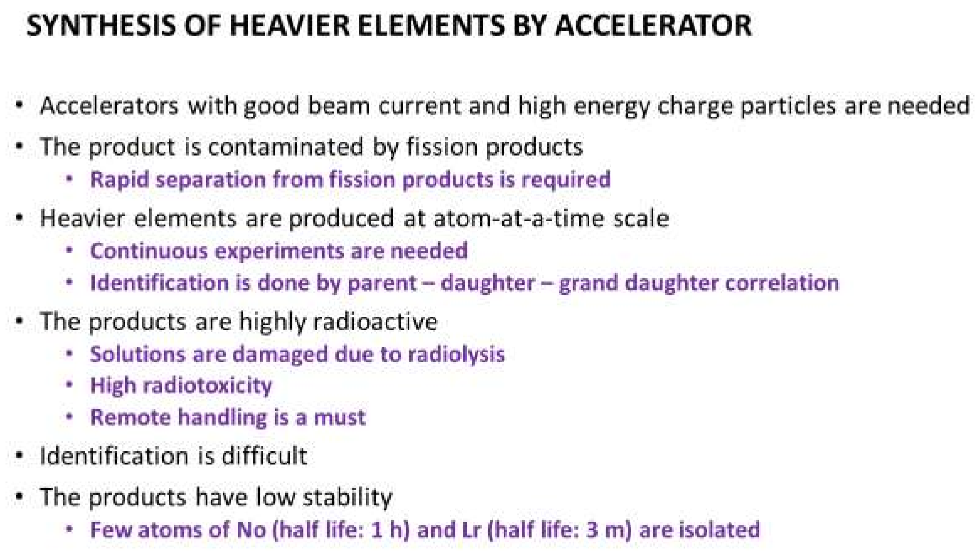
$${}^{238}_{92}U + {}^{2}_{1}D \longrightarrow {}^{238}_{93}Np + 2\,{}^{1}_{0}n \qquad {}^{238}_{93}Np \xrightarrow[2.117\ d]{\beta^-} {}^{238}_{94}Pu$$

$${}^{249}_{98}Cf + {}^{11}_{5}B^{5+} \longrightarrow {}^{256}_{103}Lr + 4\,{}^{1}_{0}n$$

This is how heavy actinides and trans-actinides are made

Isotope	$T_{1/2}$	Amt/y
^{248}Cm	3.5x10^{5}y	150 mg
^{249}Bk	320 d	50 mg
^{252}Cf	2.64 y	500 mg
^{253}Es	20.3 d	2 mg
^{257}Fm	100 d	1 pg

Now as I mentioned, the other actinides also can be synthesized in the reactor by neutron capture. We have just mentioned about how protactinium is formed in the reactor. Also, I will show here how neptunium-239 is formed in a reactor by irradiating ^{238}U by a neutron which produces ^{239}U and it undergoes a beta decay to give ^{239}Np which has 2.3 days half life and it is converted to ^{239}Pu again by a beta decay. This plutonium-239 can undergo alpha decay to give ^{235}U. So, this is a general decay series of this ^{238}U if it is undergoing a neutron capture. Also, this ^{238}U can undergo neutron capture (fast neutron) to give ^{237}U by a (n,2n) reaction and which again decays by beta decay to ^{237}Np. ^{237}Np is very important because it has a very long half life and once it is produced in the reactor it goes mostly to the waste stream as a minor actinide it has a very significant repercussion in the radioactive waste management because of the very long half-life of 2.1x10^{6} years. ^{237}Np is also produced in the reactor by ^{235}U capturing a neutron giving ^{236}U which by another neutron capture gives ^{237}U and by beta decay it gives ^{237}Np. So, these are the ways this ^{237}Np is produced. Also, some of the relatively heavier actinides like americium and curium are produced by neutron bombardment like ^{239}Pu with 4 neutrons it gives ^{243}Pu and then by a beta decay it gives ^{243}Am which can capture a neutron to give ^{244}Am and which again undergoes beta decay to give ^{244}Cm. So, this is how americium and curium can be produced in the nuclear reactors. Now for high yield, we need actually high neutron flux as I have already mentioned in the previous lecture that thermonuclear explosion when carried out einsteinium and fermium were detected and that is how these elements were discovered and also if you take ^{239}Pu and you irradiate in a reactor with a very high neutron flux like $3x10^{14}$ n/cm^{2}/s then you need years of irradiation for producing even 1 milligram of californium-252. I have given here some of the actinides which are produced in the reactor by irradiation and you can see that ^{248}Cm is formed around 150 milligram and ^{249}Bk is formed only 50 milligram under the same conditions and ^{252}Cf you get 500 milligram; ^{253}Es only 2 milligram and ^{257}Fm only 1 picogram. So, this is because of this reaction cross sections are also less and also the $t_{1/2}$ (half life) of this radio nuclides of the actinides (you can see here) is very less so that is how it is decaying. For 248 curium it ($t_{1/2}$) is $3.5x10^{5}$ years whereas for ^{253}Es it is only 20 days and for ^{257}Fm it is only 100 days so that is how it decays also the heavier actinides and the amount also is less because of the very low neutron capture cross sections. There is also the actinide synthesis can be done by charged particle bombardment for example ^{238}Pu is synthesized by deuterium bombardment of ^{238}U the reaction is given in the slide where, ^{238}U and deuterium react to get ^{238}Np which undergoes a beta decay with a 2.1 days half-life to ^{238}Pu. This is a reaction actually which was used as I mentioned in the previous lecture for plutonium production for the first time in the Berkeley Radiation Laboratory. Now, similarly this californium also can undergo charged particle bombardment like $^{11}B_5^{+}$ ion beam to give ^{256}Lw and also 4 neutrons are emitted. This is how the heavy actinides and the transactinides are made by the bombardment of charged particle This will be covered in a more detail when I am discussing about the transactinides. Now I will summarize here this heavier actinide elements synthesis by accelerators.

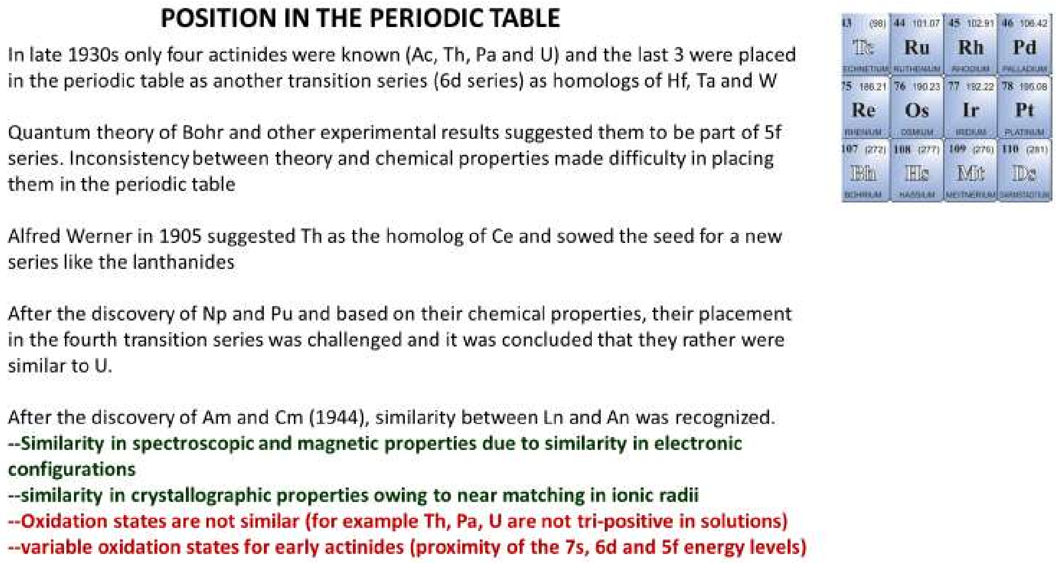


SYNTHESIS OF HEAVIER ELEMENTS BY ACCELERATOR

- Accelerators with good beam current and high energy charge particles are needed
- The product is contaminated by fission products
  - Rapid separation from fission products is required
- Heavier elements are produced at atom-at-a-time scale
  - Continuous experiments are needed
  - Identification is done by parent – daughter – grand daughter correlation
- The products are highly radioactive
  - Solutions are damaged due to radiolysis
  - High radiotoxicity
  - Remote handling is a must
- Identification is difficult
- The products have low stability
  - Few atoms of No (half life: 1 h) and Lr (half life: 3 m) are isolated

So, the accelerators, when used, should have good beam current and high energy charged particles. The product many times is contaminated by the fission product with the fission reaction will be taking place to a much larger extent than this production of the heavier actinides. So that is how this separation of this heavier actinides from the fission product is required. Also, if you go to very heavy actinides or even transactinides their atom at a time scale these elements of the nuclei are formed. So, that is how these continuous experiments are needed. If you want to carry out some of these experiments, particularly the chemistry studies, online runs have to be done when these experiments at an atom-at-a-time scale of these actinides are produced and this has to be transported to the adjacent laboratory where this experiment has to be carried out and there continuously these experiments need to be carried out because otherwise they are decaying. And their identification is done by parent, daughter and the granddaughter correlation where you have one particular actinite A which is decaying to B and which is decaying to C. As A has a very short half life you when you carry out the experiment you cannot probably detect A but B and C will be in significant quantities. So by detecting B and C you can always say that this well A has also formed and that is how the chemistry of A has been established. The products are also highly radioactive because of their very small half-lives and because of that the solutions are damaged due to radiolysis.

These have very high radio toxicity and also because of this, remote handling is a requirement for this type of experiments. Identification as I said it is difficult because you have a host of fission products which also are formed. So, identification is difficult and they need to separate from the fission products and then identify these radionuclides (actinide isotopes). The products also have a very low stability as I have already mentioned in case of the nobelium isotope. You can see here even nobelium with a half life of one hour or lawrencium with a half-life of three minutes they are isolated but then because of the low stability we have to carry out the chemistry very fast.



POSITION IN THE PERIODIC TABLE

In late 1930s only four actinides were known (Ac, Th, Pa and U) and the last 3 were placed in the periodic table as another transition series (6d series) as homologs of Hf, Ta and W

Quantum theory of Bohr and other experimental results suggested them to be part of 5f series. Inconsistency between theory and chemical properties made difficulty in placing them in the periodic table

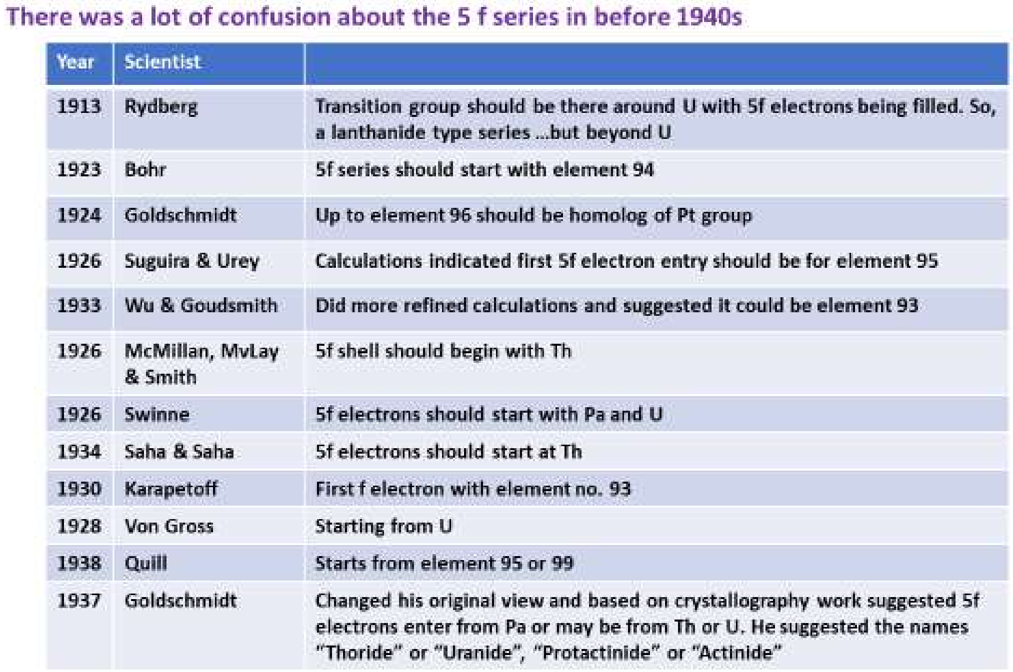
Alfred Werner in 1905 suggested Th as the homolog of Ce and sowed the seed for a new series like the lanthanides

After the discovery of Np and Pu and based on their chemical properties, their placement in the fourth transition series was challenged and it was concluded that they rather were similar to U.

After the discovery of Am and Cm (1944), similarity between Ln and An was recognized.
--Similarity in spectroscopic and magnetic properties due to similarity in electronic configurations
--similarity in crystallographic properties owing to near matching in ionic radii
--Oxidation states are not similar (for example Th, Pa, U are not tri-positive in solutions)
--variable oxidation states for early actinides (proximity of the 7s, 6d and 5f energy levels)

Now coming to the position in the periodic table. In the late 1930s only four actinides were known that is actinium, thorium, protactinium and uranium and the last three were placed in the periodic table as another transition series that is the 6d transition series as the homologs of hafnium, tantalum and tungsten. Now, as I have already mentioned in the chemistry of neptunium how the neptunium was placed under rhenium. So, because of this particular positioning in the periodic table to the 6d transition series this was suggested that time. However, the quantum theory of Bohr and other experimental results suggested that these actinides instead of being the 6d series they may be part of the 5f series and also the inconsistency between the theory and chemical properties made it difficult in placing them in the periodic table. So, there was a lot of confusion I will be showing in the next slide how this confusion was actually cleared. Then Alfred Werner in 1905 suggested that thorium as the homolog of cerium because thorium and cerium their chemistry very much comparable and he sowed the seed for a new series like the lanthanides. After the discovery of neptunium and plutonium and based on their chemical properties, their placement in the 4th transition series was challenged and it was concluded that neptunium and plutonium had their chemistry as more similar to that of uranium rather than that of rhenium and osmium. So, after the discovery of americium and curium by Seaborg's group in 1944 the similarity between lanthanide and actinide was recognized because americium and curium both behaved as trivalent metal ions and the similarity in the spectroscopic and magnetic properties also was due to the similarity in the electronic configuration. I will be discussing the electronic configuration shortly.

Similarly, in the crystallographic properties, when you do the near matching in the ionic radii of these actinides to that of the lanthanides also suggested that they may be similar to the lanthanides. Oxidation states however are not similar to that of the lanthanides like thorium, protactinium and uranium they are not tri-positive in solutions but they are plus 4, plus 5 and plus 6 oxidation states. Variable oxidation states for the early actinides also have been detected but then the reason for this will be because of the 7s, 6d and 5f energy levels are very close in their energies so that is how the variable oxidation states of the actinides were explained. Now as I was mentioning there were a lot of confusion actually about the 5f series before the 1940s. So, I will list down here how different groups were proposing the position of actinides or where the 5f series will be starting.



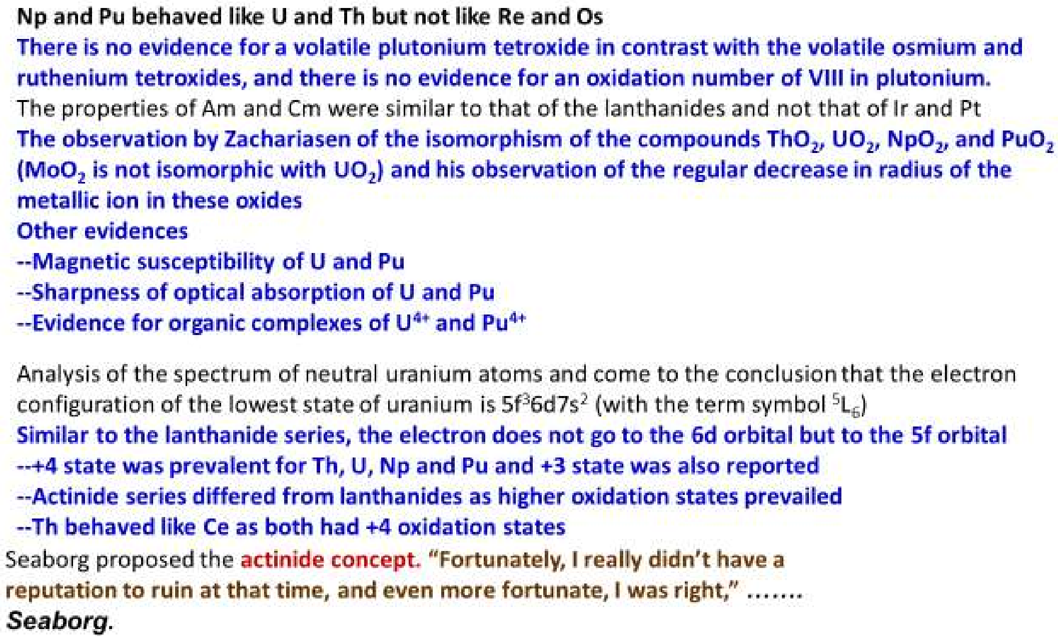
There was a lot of confusion about the 5 f series in before 1940s

Year	Scientist	
1913	Rydberg	Transition group should be there around U with 5f electrons being filled. So, a lanthanide type series ...but beyond U
1923	Bohr	5f series should start with element 94
1924	Goldschmidt	Up to element 96 should be homolog of Pt group
1926	Suguira & Urey	Calculations indicated first 5f electron entry should be for element 95
1933	Wu & Goudsmith	Did more refined calculations and suggested it could be element 93
1926	McMillan, MvLay & Smith	5f shell should begin with Th
1926	Swinne	5f electrons should start with Pa and U
1934	Saha & Saha	5f electrons should start at Th
1930	Karapetoff	First f electron with element no. 93
1928	Von Gross	Starting from U
1938	Quill	Starts from element 95 or 99
1937	Goldschmidt	Changed his original view and based on crystallography work suggested 5f electrons enter from Pa or may be from Th or U. He suggested the names "Thoride" or "Uranide", "Protactinide" or "Actinide"

1913, Rydberg proposed that the transition groups would be there around uranium with 5f electrons being filled. So, a lanthanide type of series but beyond uranium. In 1923, Bohr suggested that 5f series should start with element 94 and in 1924 Goldschmidt, proposed that up to 96 should be homolog of the platinum group and beyond that only there can be the 5f series. In 1926, Suguira and Urey have done calculations and indicated that the first 5f electron entry should be for element 95. In 1933, Wu and Goudsmith did more refined calculations and suggested that the first 5f electron filling should be not for element 95 but for element 93.

In 1926 McMillan, MvLay and Smith suggested that a 5f shell should start with thorium and in 1926 again Swinne suggested that 5f electrons should start with protactinium and uranium. In 1934, Saha and Saha suggested the 5f electrons should start at thorium and in In 1930, Karapetoff suggested the first 5f electron with element number 93. So, as you can see here that many people suggested that it should be at 93 or 94 and some even 95. Subsequently, in 1928, Van Gross suggested that again it will be starting from element 92 that is uranium and 1938 Quill suggested that it starts from 95 or 99. So, he has increased to the heavier actinides. In 1937, Goldschmidt changed his original view and based on the crystallography work suggested that the 5f electrons enter from protactinium or maybe thorium or uranium. So, he suggested the name actinide and also, he suggested other alternative names like thoride, uranide or protactinide. Now what is the major objection coming to that is the neptunium and plutonium behave like uranium and thorium but not like rhenium and osmium which is there in the periodic table for the 6d series. Now, there is no evidence for the volatile plutonium tetroxide in contrast with the volatile osmium and ruthenium tetroxides and also there is no evidence for an oxidation number of 8 in case of plutonium. So, they suggested that the plutonium is definitely not behaving like osmium.

The observation of Zachariasen on the isomorphism of the compounds viz. thorium dioxide, uranium dioxide, neptunium dioxide and plutonium dioxide suggested that uranium dioxide is not isomorphic to molybdenum dioxide and his observation of the regular decrease in the radius of the metallic ion in these oxides also suggested that this is a separate series similar to the lanthanide series. Other evidences are the magnetic susceptibility of uranium and plutonium, sharpness of the optical absorption of uranium and plutonium, evidence of organic complexes of uranium 4 plus and plutonium 4 plus. Also, the analysis of the spectrum of the uranium atom come to the conclusion that the electronic configuration of the lowest state of uranium is $5f^3 6d^1 7s^2$ with the term symbol $^5L_6$. Similar to the lanthanide series, the electron does not go to the 6d orbital but to the 5f orbital. Now the plus 4 state was prevalent for thorium, uranium, neptunium and plutonium. The last 3 under the reducing condition and also the plus 3 state was also reported for uranium, neptunium and plutonium under the suitable reducing conditions.



Np and Pu behaved like U and Th but not like Re and Os

There is no evidence for a volatile plutonium tetroxide in contrast with the volatile osmium and ruthenium tetroxides, and there is no evidence for an oxidation number of VIII in plutonium.

The properties of Am and Cm were similar to that of the lanthanides and not that of Ir and Pt

The observation by Zachariasen of the isomorphism of the compounds ThO_2, UO_2, NpO_2, and PuO_2 (MoO_2 is not isomorphic with UO_2) and his observation of the regular decrease in radius of the metallic ion in these oxides

Other evidences

--Magnetic susceptibility of U and Pu

--Sharpness of optical absorption of U and Pu

--Evidence for organic complexes of U^{4+} and Pu^{4+}

Analysis of the spectrum of neutral uranium atoms and come to the conclusion that the electron configuration of the lowest state of uranium is $5f^3 6d 7s^2$ (with the term symbol $^5L_6$)

Similar to the lanthanide series, the electron does not go to the 6d orbital but to the 5f orbital

--+4 state was prevalent for Th, U, Np and Pu and +3 state was also reported

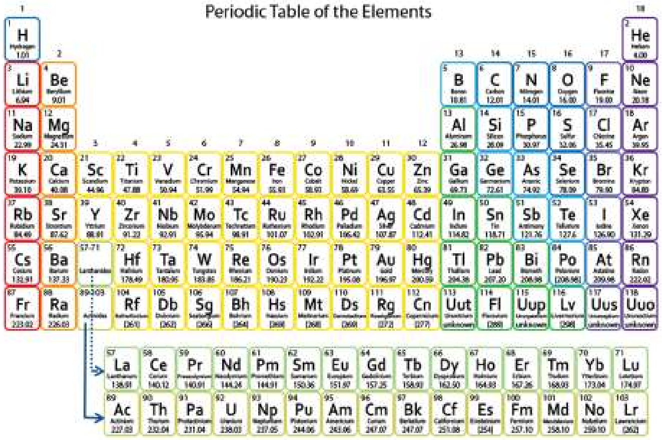
--Actinide series differed from lanthanides as higher oxidation states prevailed

--Th behaved like Ce as both had +4 oxidation states

Seaborg proposed the **actinide concept.** **"Fortunately, I really didn't have a reputation to ruin at that time, and even more fortunate, I was right," …….** ***Seaborg.***

The actinide series differed from the lanthanides as the higher oxidation states prevailed in case of the lighter actinides and thorium behaved like cerium as both have the plus 4 oxidation states. With this background and also the discovery of americium and curium by Seaborg and their chemistry studies suggested that they were more like the lanthanides rather than like the transition elements. So, Seaborg was tempted to propose this actinide concept and he has sent a publication that time suggesting his "actinide concept" and his colleagues advised against this because they said that this was a very wild idea and you cannot have an actinide series similar to the lanthanides as Seaborg was proposing. They said that your reputation will be ruined but Seaborg said that I didn't have that much reputation at that time and I was also more fortunate that I was right. Ultimately, he was proven right that there was actinide series similar to the lanthanides.

Position of actinides in Periodic Table

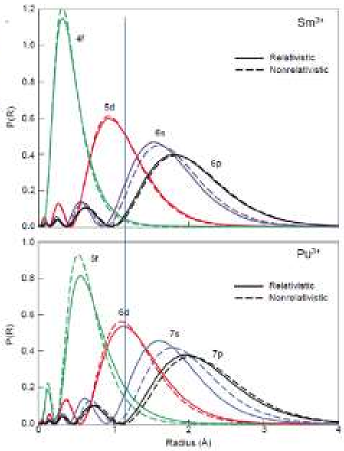


Now coming to the position in the periodic table, as I have mentioned before this, the actinides initially are proposed to be under this fourth transition series. However, after Seaborg's proposition this was the actinide series where thorium is also just below cerium and protactinium below praseodimium. However, this behavior of the lanthanides was entirely different because they are all plus three oxidation states and for actinides only beyond americium you have the plus three oxidation state. Now coming to differences between the actinides and lanthanides.

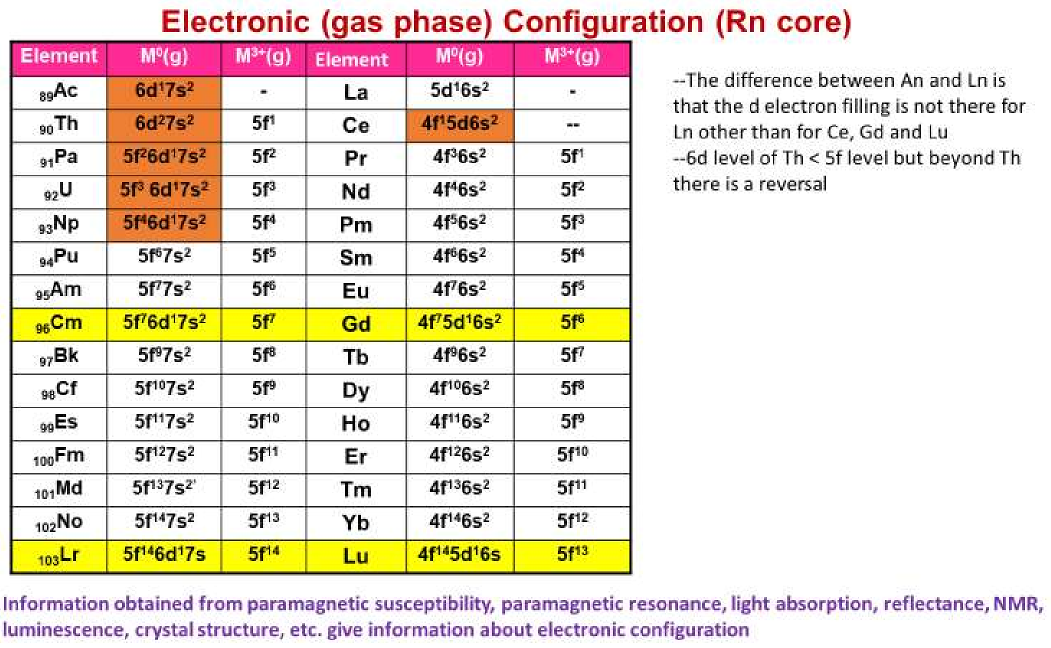
Difference between Actinides and Lanthanides

- **Lanthanides: Naturally occurring except Pm.**
- **Actinides: Man made except Ac, Th, Pa, U.**
- **Difference in energy between 5f & 6d orbitals of actinides are less than 4f & 5d orbitals of lanthanides.**
- **5f orbitals of actinides have greater spatial extension and hence participate in bonding.**

Participation of '5f' electrons in bonding makes the chemistry of actinides much richer than that of lanthanides



Lanthanides are naturally occurring except for promethium and actinides and man-made except for actinium, thorium, protactinium and uranium. There is a difference in energy between 5f and 6d orbitals of actinides which are less than that of the 4f and 5d orbitals of the lanthanides. The 5f orbitals of the actinides have greater spatial extension and hence, participate in the bonding. Some cases even covalent bondings are reported for the actinides and that is the basis of the lanthanide-actinide separation which I will be discussing in a future lecture. Now coming to this electronic configuration of the actinides.



Electronic (gas phase) Configuration (Rn core)

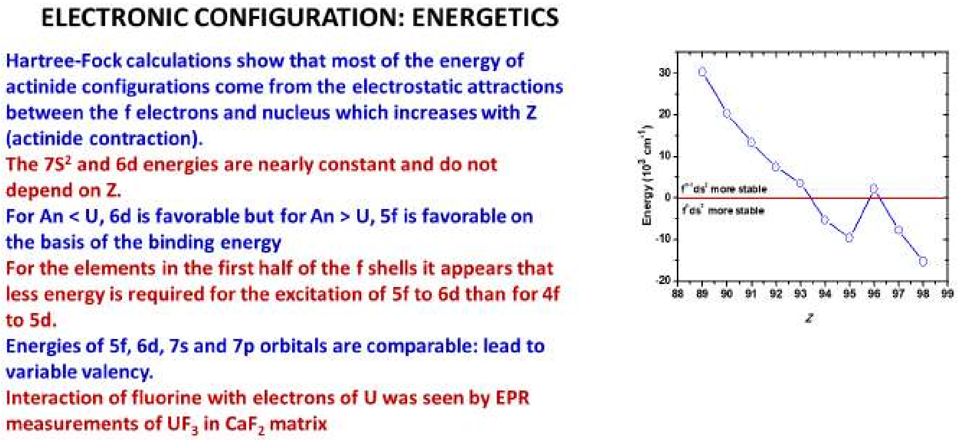
Element	$M^0(g)$	$M^{3+}(g)$	Element	$M^0(g)$	$M^{3+}(g)$
$_{89}$Ac	$6d^17s^2$	-	La	$5d^16s^2$	-
$_{90}$Th	$6d^27s^2$	$5f^1$	Ce	$4f^15d6s^2$	--
$_{91}$Pa	$5f^26d^17s^2$	$5f^2$	Pr	$4f^36s^2$	$5f^1$
$_{92}$U	$5f^3 6d^17s^2$	$5f^3$	Nd	$4f^46s^2$	$5f^2$
$_{93}$Np	$5f^46d^17s^2$	$5f^4$	Pm	$4f^56s^2$	$5f^3$
$_{94}$Pu	$5f^67s^2$	$5f^5$	Sm	$4f^66s^2$	$5f^4$
$_{95}$Am	$5f^77s^2$	$5f^6$	Eu	$4f^76s^2$	$5f^5$
$_{96}$Cm	$5f^76d^17s^2$	$5f^7$	Gd	$4f^75d^16s^2$	$5f^6$
$_{97}$Bk	$5f^97s^2$	$5f^8$	Tb	$4f^96s^2$	$5f^7$
$_{98}$Cf	$5f^{10}7s^2$	$5f^9$	Dy	$4f^{10}6s^2$	$5f^8$
$_{99}$Es	$5f^{11}7s^2$	$5f^{10}$	Ho	$4f^{11}6s^2$	$5f^9$
$_{100}$Fm	$5f^{12}7s^2$	$5f^{11}$	Er	$4f^{12}6s^2$	$5f^{10}$
$_{101}$Md	$5f^{13}7s^{2'}$	$5f^{12}$	Tm	$4f^{13}6s^2$	$5f^{11}$
$_{102}$No	$5f^{14}7s^2$	$5f^{13}$	Yb	$4f^{14}6s^2$	$5f^{12}$
$_{103}$Lr	$5f^{14}6d^17s$	$5f^{14}$	Lu	$4f^{14}5d^16s$	$5f^{13}$

--The difference between An and Ln is that the d electron filling is not there for Ln other than for Ce, Gd and Lu

--6d level of Th < 5f level but beyond Th there is a reversal

Information obtained from paramagnetic susceptibility, paramagnetic resonance, light absorption, reflectance, NMR, luminescence, crystal structure, etc. give information about electronic configuration

As I have shown here, starting from actinium to lawrencium see the electronic configurations and also for comparison purpose, I have put the electronic configurations of the lanthanides. You can see here that for lanthanides only for cerium, gadolinium and lutetium you have the d-electrons and for all others you find that the f-electrons are getting filled. On the other hand for the actinides you can see that the initial actinides up to neptunium you have the d-electrons and the f-electrons are also there. Now beyond neptunium you have this plutonium and americium there you do not have the d-electrons and apart from curium you have all other actinides again with only the f-electrons getting filled gradually. So, this is a similarity of the actinides with the lanthanides starting from plutonium but the early actinides as I have already mentioned because of the comparable energy levels of the 5 f, 6 d and the 7 s levels.



ELECTRONIC CONFIGURATION: ENERGETICS

Hartree-Fock calculations show that most of the energy of actinide configurations come from the electrostatic attractions between the f electrons and nucleus which increases with Z (actinide contraction).

The $7S^2$ and 6d energies are nearly constant and do not depend on Z.

For An < U, 6d is favorable but for An > U, 5f is favorable on the basis of the binding energy

For the elements in the first half of the f shells it appears that less energy is required for the excitation of 5f to 6d than for 4f to 5d.

Energies of 5f, 6d, 7s and 7p orbitals are comparable: lead to variable valency.

Interaction of fluorine with electrons of U was seen by EPR measurements of UF_3 in CaF_2 matrix

So that is this type of configurations are possible. Now just coming to the electronic configuration also here you can see I have given this figure where you see that this comparison of $f^{(n-1)}d\ s^2$ and f^ns^2. These two electronic configurations are compared as you see here, the $f^{(n-1)}ds^2$ is more stable up to the element number 93 that is neptunium and beyond that like the plutonium you have this f^ns^2 type of configuration. And then americium and up to the curium again you have this $f^{(n-1)}ds^2$ type of configuration and beyond curium again you have this configuration where you have f^ns^2 which is more stable. So, this is what I would like to cover here in this electunium configuration and we will discuss more about this chemistry of actinides in the subsequent lectures. Thank you.

Contact Detail:
Email: mpatra@barc.gov.in
Phone: 022-25594576