Course Name: Nuclear and Radiochemistry
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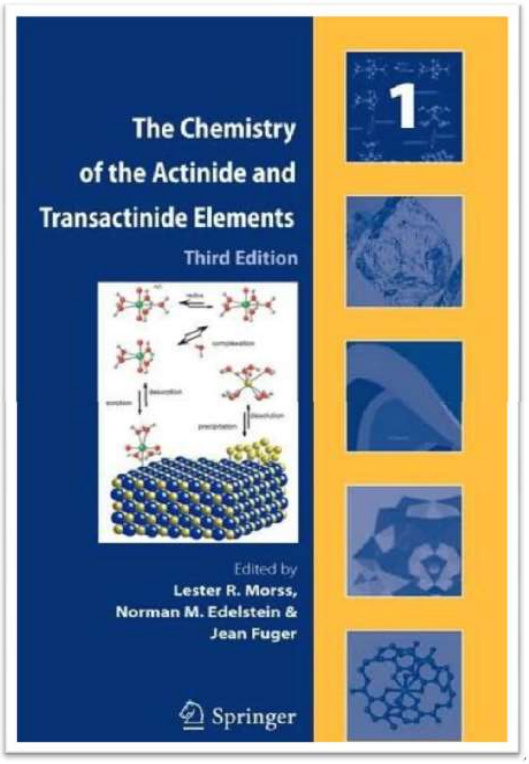
Department Name: Radiochemistry Division
Institute Name: Homi Bhabha National Institute
Week - 09
Lecture - 43

Hello everyone, welcome to the series of lectures on actinide chemistry, todaywe are going to discuss the chemistry of f-block elements that is lanthanide and actinides.Before the lecture, I just assumed that most of you had gone through the other lectures on actinide chemistry in which the basic ideas of the actinide concept, their position in the periodic table, and their electronic configuration are already discussed.So, I will not go into the details of those concepts.



References/Sources

Chapter 15.
Summary and Comparison of Properties of the Actinide and Transactinide Elements
Norman M. Edelstein, Jean Fuger, Joseph J. Katz, and Lester R. Morss

Chapter 23:
Actinides In Solution: Complexation And Kinetics
Gregory R. Choppin And Mark P. Jensen

Speciation plot: Medusa/Hydra from KTH

Some information and images: Internet/web

So, first, I just want to add that these books that I have used for my references and some of the sources that I have taken from the internet. So, I have used primarily this book which is the Chemistry of Actinides and Transactinide Elements for my reference in which I have generally considered chapter that is chapters 15 and chapter 23.I have used Medusa Hydra-

based software for the speciation plots. I have also taken some information from the internet and the web for my presentation.

Electronic configuration : Derived from spectroscopic studies

Element	M	M^{3+}	Element	M	M^{3+}
Ac	$6d^17s^2$	-	La	$5d^16s^2$	-
Th	$6d^27s^2$	$5f^1$	Ce	$4f^15d^16s^2$	$4f^1$
Pa	$5f^26d^17s^2$	$5f^2$	Pr	$4f^36s^2$	$4f^2$
U	$5f^3\ 6d^17s^2$	$5f^3$	Nd	$4f^46s^2$	$4f^3$
Np	$5f^46d^17s^2$	$5f^4$	Pm	$4f^56s^2$	$4f^4$
Pu	$5f^67s^2$	$5f^5$	Sm	$4f^66s^2$	$4f^5$
Am	$5f^77s^2$	$5f^6$	Eu	$4f^76s^2$	$4f^6$
Cm	$5f^76d^17s^2$	$5f^7$	Gd	$4f^75d^16s^2$	$4f^7$
Bk	$5f^97s^2$	$5f^8$	Tb	$4f^96s^2$	$4f^8$
Cf	$5f^{10}7s^2$	$5f^9$	Dy	$4f^{10}6s^2$	$4f^9$
Es	$5f^{11}7s^2$	$5f^{10}$	Ho	$4f^{11}6s^2$	$4f^{10}$
Fm	$5f^{12}7s^2$	$5f^{11}$	Er	$4f^{12}6s^2$	$4f^{11}$
Md	$5f^{13}7s^2$	$5f^{12}$	Tm	$4f^{13}6s^2$	$4f^{12}$
No	$5f^{14}7s^2$	$5f^{13}$	Yb	$4f^{14}6s^2$	$4f^{13}$
Lr	$5f^{14}6d^17s$	$5f^{14}$	Lu	$4f^{14}5d^16s^2$	$4f^{14}$

So, as you already know about the electronic configuration of lanthanides and actinides just to brief you or just to start the presentation, I have shown you the electronic configuration of actinides and the electronic configuration of lanthanides.If you see, I have also given you the electronic configuration of the trivalent lanthanides and actinides.If you see, the lanthanides and actinides, what we find common in the two is that in actinides when you talk about the tri-positive state, the f-electron filling goes from $4f^{l}$ to $4f^{14}$ anda very similar case arises when you talk about the electronic configuration of thelanthanides from $4f^{l}$ to $4f^{14}$.

So, when you see the tri-positive starting from f^1 to f^{14} filling is there but when you talk about the atoms rather than this tri-positive state, you can find certain differences.Suppose this one.So, why does this kind of difference arise?Most of these things have been already discussed So, I will not go into detail but, one thingI just want to convey to you is that, if you see this, there the occupancy of d-orbitals is there.It suggests that the f- and d-orbitals are close to each other but after that,if you see the electronic configuration prefer the f and $7s^2$ kind of system. You can see, generally that if you talk about the actinide then $5f^n$ $6d^1$ and $7s^2$.

This kind of electronic configuration is preferred when n is equal to 2 to 4 but, when you go beyond n equal to 6, what is there?The most preferred configuration is $5f^n$ $6d^0$ and $7s^2$.So, this preference goes up to americium and after that, you can again see the involvement of d-orbital that comes from the half-filled shell that is $4f^7$ and $5f^7$.

Comparison of Lanthanides and Actinides

- Element No. 89-103: Ac – Lr
- Strong resemblance with Lanthanides (La-Lu)
- Lanthanides: 14 4f electrons from Ce
- Actinides: 14 5f electrons from Pa
- Lanthanides: Naturally occurring except Pm (a f.p.)
- Actinides: Man made except Ac, Th, Pa, U

58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Similarities	Differences
f-obital as part of active valence orbital	5f orbital of An are in close energetic proximity to other valence orbitals
Ln/An contraction	6d orbital are energetically accessible
Gd^{3+}:Cm^{3+} (f^7 configuration)	4f electrons shielded more effectively than 5f electrons
Trivalent state: Similar chemical properties	Variable valency in Actinides

With this basic understanding of electronic configuration, we would like to see some of the differences and similarities between lanthanides and actinides.If you all know that when we talk about the actinides and lanthanides, the actinides start from Actinium and end at Lawrencium whereas, when we talk about the lanthanides, they start fromLanthanum and end at Lutetium.The filling of f-electrons starts at cerium in the case of lanthanide whereas the filling of f-electrons starts at protactinium in the case of actinides.

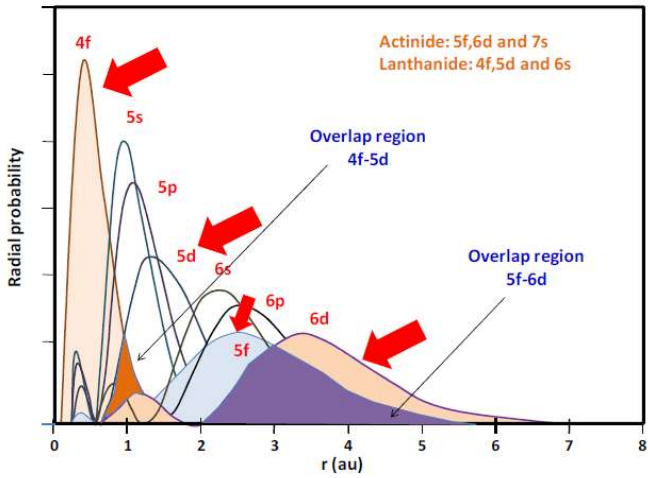
Most of the lanthanides are naturally occurring except Promethium which is a fission product whereas actinides are generally man-made and only a few of them such as Actinium, Thorium, Protactinium, and uranium occur in nature. So, when you talk about the similarities as we have seen in the electronic configuration, both lanthanides and actinides use f-orbital as a part of active valence orbital.Both lanthanides and actinides

when going from the left-hand side to the right-hand side when you move like this, there is a decrease in the size.So, that is basically due to contraction.

So, we say this as a lanthanide contraction in the case of lanthanide and an actinide contraction in the case of actinides.We will try to discuss this again in the upcoming slide.When you see the tri-positive metal ion, if you see these two, they have an f^7 configuration.in both Gadolinium and Curium and the trivalent state whether this or this, they behave in very similar ways when you talk about the trivalent state in both lanthanide and actinide. But what the difference is?

Radial Distribution of different orbitals

Element	M	M^{3+}	Element	M	M^{3+}
Pa	$5f^2 6d^1 7s^2$	$5f^2$	Pr	$4f^3 6s^2$	$4f^2$
U	$5f^3\ 6d^1 7s^2$	$5f^3$	Nd	$4f^4 6s^2$	$4f^3$
Np	$5f^4 6d^1 7s^2$	$5f^4$	Pm	$4f^5 6s^2$	$4f^4$



Differences
6d orbital are energetically accessible
5f orbital of An are in close energetic proximity to 6d and 7s orbitals
4f electrons shielded more effectively than 5f electrons
Variable valency in Actinides

Several differences mainly arise because the lanthanides use 4f whereas actinides use 5f (orbitals).The main difference is that they are using different kinds of shells.The first difference you can say is that 6d orbitals are energetically accessible (in actinides).What does it mean that as I have shown you in the previous slides if you start filling electrons in the early elements of actinide versus lanthanide, you can see there are no d orbitals.Whereas

there are d orbitals.What it suggests is that the f- and d- (orbitals) are close, they are energetically very close.

So, in actinides, these three orbitals that are 5f, 6d, and 7s, are energetically very close. I have written in the next slide that 5f orbitals of actinides are in close energetic proximity to the 6d and 7s orbitals. Whereas if you talk about the 4f electrons, they are shielded more effectively than the 5f electron that you can see from this graph also. This is the 4f, this is the 5f. So, if you see there, 5f is more diffused compared to 4f. And if you see the energy difference between 4f and 5d (thick red arrows) and if you see the 5f and 6d.

If you see 5f is here, 6d is here (thick red arrows). They have quite a good amount of overlap (violet region). But when you see the other one which is the 4f and the corresponding 5d, the overlap is very small (orange region). So, this makes their energy very close to each other. Similarly, when we talk about the valency of these actinides these three (5f, 6d, and 7s) are very close to each other. So, you can remove electrons either from s, either from s or d or f. But because of this, they show variable oxidation states in the aqueous media. So, let us see something about their oxidation state.

Oxidation States

58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
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*f^1	f^2	f^3	f^4	f^5	f^6	f^7	f^8	f^9	f^{10}	f^{11}	f^{12}	f^{13}	f^{14}

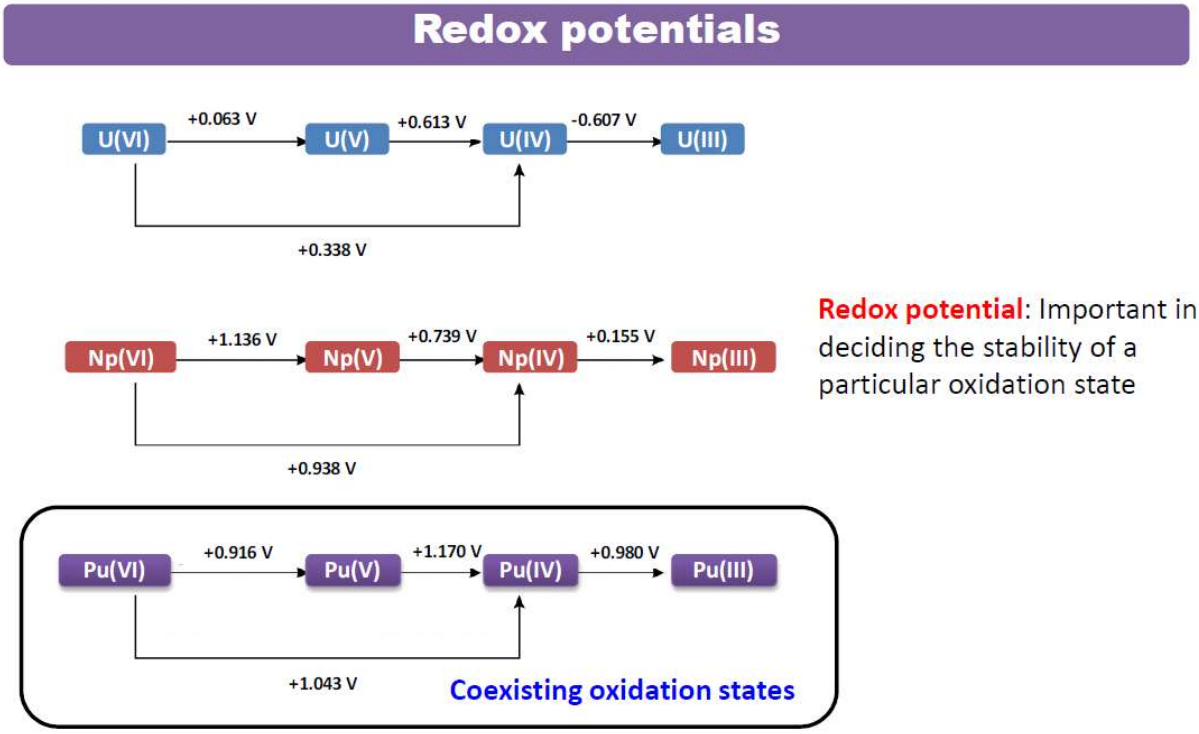
* M^{3+} ion configuration

Group oxidation state of lanthanides : +3

O.S	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
2							(2)			(2)	(2)	2	2	2	
3	3	(3)	(3)	3	3	3	3	3	3	3	3	3	3	3	3
4		4	4	4	4	4	4	4	4	(4)					
5			5	5	5	5	5								
6				6	6	6	6								
7					7	7									

• Underlined: Stable oxidation state
• No. in bracket: Reported in solid state

So, when you talk about these lanthanides, they have a group oxidation state of 3. What does it mean? that most of the lanthanides have only an oxidation state of 3. But if you see the actinides, you can start from 3, 4, 5, 6, 7, and sometimes 2 also.You can see when you talk about the actinides, the oxidation states vary from plus 2 to plus 7, whereas when you talk about the lanthanides, it is mainly plus 3.Why is it like so?Even one more peculiarity about the actinides is the existence of multiple oxidation states at a single time.For example, in plutonium, you can see most of the oxidation state in the case of plutonium exists at the same time in the solution. How it is possible? to understand that, let us see the redox potential of these actinides in the solution phase.



Formal reduction potential for uranium, neptunium and plutonium at 1 M $HClO_4$

CHAPTER 23: Actinides In Solution: Complexation And Kinetics
Gregory R. Choppin And Mark P. Jensen

So, here I have given you the redox potential of uranium, neptunium, plutonium, and the corresponding couple such as U(VI) to U(V), U(V) to U(IV), and U(IV) to U(III).And this all is in one molar perchloric acid.If you look very carefully, the first couple (U(VI) to U(V)) has a reduction potential of +0.06.The next couple (U(V) to U(IV)) is almost 10 times higher.

And the next one (U(IV) to U(III)) is again going in the negative direction. There is a huge difference (when going from) U(VI) to U(III) couples. When you see the neptunium case, again you can see the Np (VI) (to Np(V)) is plus 1.136 whereas Np(V) to Np (IV) is 0.739. And again, it is getting reduced to 0.155 in the case of Np (IV) to Np (III) So, again you can see there is a difference. What about plutonium? The first one is from Pu (VI) to Pu(V) is 0.916. The second one (Pu(V) to Pu (IV)) is hardly 0.25 units ahead which is 1.170 V. The Third one (Pu (IV) to Pu (III))) is very close again 0.98. so even if this one is directly going from Pu (VI) to Pu (IV), again it is in the range of 1.043. What it

means is that most of these redox potentials are very close to each other. What does it suggest? that most of these species can coexist at a given solution condition. So, actinides show this kind of very peculiar behavior that sometimes the co-existing oxidation states are also possible for a given element. We will now see how the individual oxidation states are varying as I have shown you that the actinide can have plus 2 to plus 7 (oxidation states). What are the elements that exist in +2 and +3, +4 to +7?

Aqueous Actinide Chemistry : Oxidation states

58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
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*f^1	f^2	f^3	f^4	f^5	f^6	f^7	f^8	f^9	f^{10}	f^{11}	f^{12}	f^{13}	f^{14}

* M^{3+} ion configuration

Divalent ions

- No(II) (E_0(No(III)/No(II))): +1.45 V *vs* NHE
- Not true for Yb (E_0(Yb(III)/Yb(II))): -1.05 V *vs* NHE

H_2O → **Radiolysis** → e^-_{aq}, $H^\bullet$, $HO^\bullet$, $HO_2^\bullet$, OH^-, H_3O^+, H_2, H_2O_2

Trivalent ions

- Am(III)-Md(III), Lr(III)
- Pu(III)- difficult and get oxidized to Pu(IV) by radiolysis products of water due to α-decay (Auto-radiolysis)→ ^{242}Pu or ^{244}Pu in 1M $HClO_4$
- Np(III) and U(III) : difficult to stabilize, require inert atmosphere
- Th(III) and Pa(III) : Not stable in solution

So first, we will talk about the divalent ion.The only possible or only actinide that prefers this state is Nobelium.You can see here, and along with this, I have given the electronic configuration in the M^{3+} state. So, it is the M^{3+} state that will give the f^{13} state. Suppose I go to M^{2+}, that will give f^{14}.So, the extra stability of this is coming because of the f^{14} configuration which is a closed-shell configuration.But the same is not true if you see the corresponding lanthanide.In lanthanide, if you see, Ytterbium it does not prefer +2, it prefers +3.That can be explained just by looking at the redox potentialIf you see the +3, the +3 to +2, that redox potential if you see it is highly positive+1.45.so energetically this

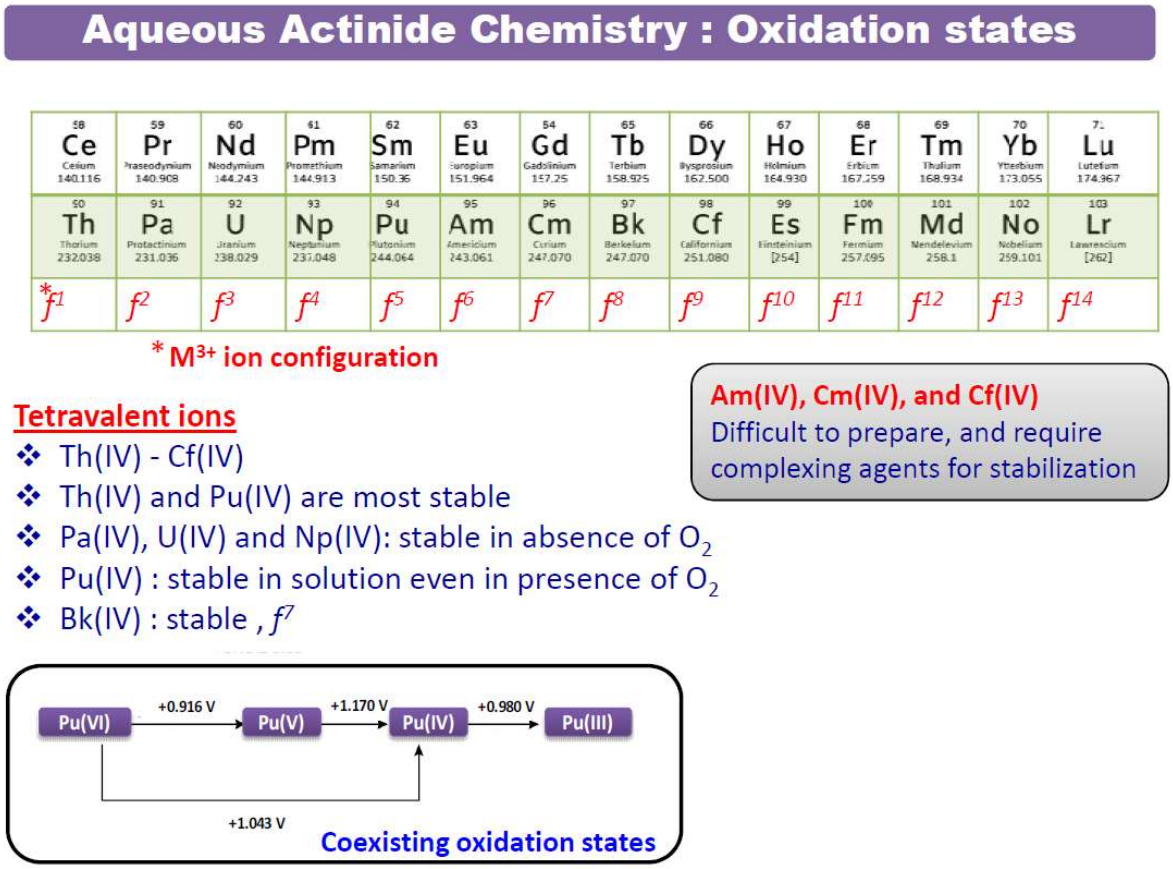
transformation is very favorable.So, the tendency of Nobelium to go to +2 from +3 is very much favorable.

But if you see the Ytterbium +3 to +2 is negative and the corresponding ΔG for this should be positive. So, this kind of transformation is very difficult. That explains why Ytterbium +2 is not stable. However, one can see that both, when we talk about the Nobelium and Ytterbium have electronic configuration, that is f^{14} when they are in the divalent state. So, what it means is that rather than the stability of f^{14}which is the closed-shell configuration there could be other factors that decide the stability of the metal ion in the aqueous phase that may be related to the relativistic effect that is very much different from the 4f orbit and the 5f orbital or due to the interaction of these orbitals into the aquatic media because of which the oxidation states differ from +2 to +3.

When we talk about the trivalent ions, starting from americium to mendelevium everything can be present in the trivalent state. So, you can see americium to mendelevium along with Nobelium can be trivalent. But if you talk about the lower part that is plutonium, neptunium, uranium, Protactinium, or Thorium there is very much difficulty in preparing the trivalent state. In plutonium, you can prepare trivalent (state) using some reducing agent but the moment you prepare they tend to oxidize to Pu (IV). Most of the time this happens because of the radiolysis of the water that will be there because when we see a plutonium solution, we know that it will give some alpha particle and this alpha particle tends to do some radiolysis and because of that radiolysis we produce several ions and several radicals that are very reactive they can be oxidizing they can be reducing.

so it happens that when we have a solution of Pu (III) which gives you continuously some alpha particle that leads to radiolysis of the water and produces this kind of very reactive species the Pu (III) gets oxidized to Pu (IV) because of the radiolysis. To confirm, what people have done that they use plutonium (isotope) that has a very large half-life such as plutonium-242 or 244, and what they have seen that when you are using thisplutonium (isotopes) where the half-life is quite large it means the alpha emission is low then their stability in the +3 (oxidation state) is quite large as compared to the other plutonium isotope where the alpha emission is very frequent or you can say is half-life is very small. When

you talk about neptunium and uraniumagain, they are very difficult to stabilize, and most of the time they require an inert atmosphere for stability. Thorium and Protactinium, are almost very difficult to form and they are not even stable in the solution phase.



Let us talk about some tetravalent ions. So, when you talk about the tetravalent, starting from Thorium to Californium everything can be prepared in the tetravalent form but if you talk about stability the most stable one is Thorium and plutonium the others are such as Protactinium, uranium, and neptunium they can be made stable but require absence of oxygen but Pu (IV) is stable and even in the presence of oxygen it is quite stable. The other actinide that is stable is Berkelium that is stable because of the f^7configuration ofthe +4 stateso that is extra stability comes because of the f^7 configuration in the case of Berkelium and as I have shown you in the previous slide, However, plutonium is stable in the +4 state but that is not the only oxidation state that is there in the plutonium solution. All the oxidation states starting from +3, +3 to +6 can coexist in the case of plutonium. When I talk about the other elements such as americium, curium, and californium they are

very difficult to prepare in the +4 and even if you try to prepare them using some redox condition you need a strong complexing agent such as chloride or phosphate to get stabilized into the +4 state.

Aqueous Actinide Chemistry : Oxidation states

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Cerium 140.116	Praseodymium 140.908	Neodymium 144.243	Promethium 144.913	Samarium 150.36	Europium 151.964	Gadolinium 157.25	Terbium 158.925	Dysprosium 162.500	Holmium 164.930	Erbium 167.259	Thulium 168.934	Ytterbium 173.055	Lutetium 174.967
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
Thorium 232.038	Protactinium 231.036	Uranium 238.029	Neptunium 237.048	Plutonium 244.064	Americium 243.061	Curium 247.070	Berkelium 247.070	Californium 251.080	Einsteinium [254]	Fermium 257.095	Mendelevium 258.1	Nobelium 259.101	Lawrencium [262]
*f^1	f^2	f^3	f^4	f^5	f^6	f^7	f^8	f^9	f^{10}	f^{11}	f^{12}	f^{13}	f^{14}

* M^{3+} ion configuration

Pentavalent ions

- Pa(V)-Am(V)
- Pa(V) and Np(V) most stable
- U(V), Pu(V) and Am(V) : unstable towards **disproportionation**

Hexavalent ions

- U(VI)-Am(VI)
- U(VI) most stable
- U(VI) >> Pu(VI) > Np(VI)

Reduction potential

U(VI)→U(V); +0.063 V

Pu(VI)→Pu(V); +0.916 V

Np(VI)→Np(V); +1.136 V

Heptavalent

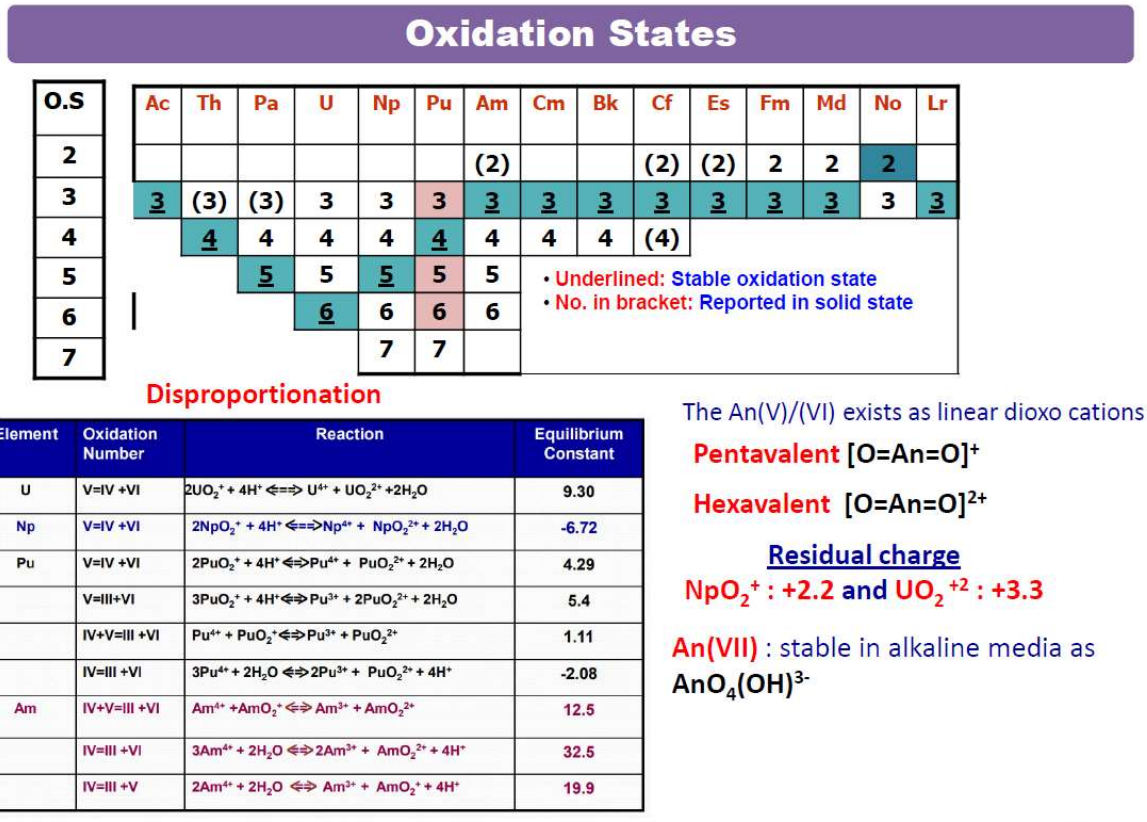
- Np(VII) and Pu(VII) in alkaline media

Let us see about the pentavalent ion again you start you can see that from protactinium to americium they can be made in the pentavalent state but the stable pentavalent is protactinium and neptunium rest all are very much unstable and most of the time this instability comes from the disproportionation.

What is disproportionation? I will just discuss this in the next slide. They are unstable concerning the disproportionation. When I talk about the hexavalent ion again from uranium to americium they all can be prepared in the hexavalent state and the most stable one is the uranium if you see uranium is stable that is because of the f^0 system if you see U(VI) doesn't have any electron in the f-orbital and if you talk about the relative stability again U(VI) is very much stable compared to Pu(VI) which is stable compared to

Np(VI) and that can directly be seen from the corresponding redox potentials If you see the reduction from U(VI) to U(V) is not very much feasible it is only 0.063 the ΔG is not very feasible but when we talk about from Np(VI) to Np(V) this is very much feasible. so that explains the trend of why Np(V) is so stable and U(VI) is so stable.

When we talk about the heptavalent state or the +(VII) states the possibility is neptunium and plutonium. That too in the alkaline medium, in the acidic medium they do not exist as a heptavalent ion. So, with this information on different kinds of oxidation states in this aquatic media let us try to see that, because as we know the stable states are from +2 to +7 in the actinide under different sets of conditions. some of them (oxidation states) have a different structure altogether.



Let us see how they differ. So, as I showed you for actinides you can have +2 to +7 (oxidation states) but ions in +(II), +(III), +(IV) are spherical. But what about +(V) and +(VI)? When you see this + (V) and + (VI) does not exist as spherical ion because here the

ionic potential of + (V) and + (VI) is so high that they abstract oxygen from the media and they make this kind of linear compound which are known as linear dioxo cations. You can see here, that for the pentavalent this actinide has a pentavalent state. You can say pentavalent, -2 on both axial oxygens so the formula charge is + i.e. AnO2+. Similarly for hexavalent,it is +2 i.e., AnO22+. So, they exist as a linear dioxo-cation but not all pentavalent.

This is mainly true for neptunium onwards. What about the pentavalent state of protactinium? This does not exist as this (linear dioxo cation). The most stable form of this is monooxy with either 1 or 2 hydroxy groups and depending on the number of hydroxy groups the oxidation (state) can be, the oxidation state of the total ion can be + 2 to +1. So, this difference exists, although this is the most stable state of Protactinium. like neptunium but this does not exist as a dioxo-cation because the formation of the dioxo-cation is very very difficult because of the symmetry of the orbitals and they cannot make these pi-bonding with the oxygen, the second oxygen basically, and they prefer to remain in this form. When I talk about the heptavalent obviously as I told you they are only stable in the alkaline media and the form in which they are stable is $AnO_4(OH)^{3-}$.

So, we know that yes these are the states and these are the basic forms. You can say that the stability forms in the aqueous phase and some of them exist as spherical and some of them exist as a linear (dioxo) ion. We say that it is a linear (dioxo) ion like this. Here, the actinyl ion and the corresponding either +1 or 2+ depending on whether they are pentavalent or hexagonal. So, let us see, as I told you that most of the time the pentavalent states are very much unstable because of the term called disproportionation.

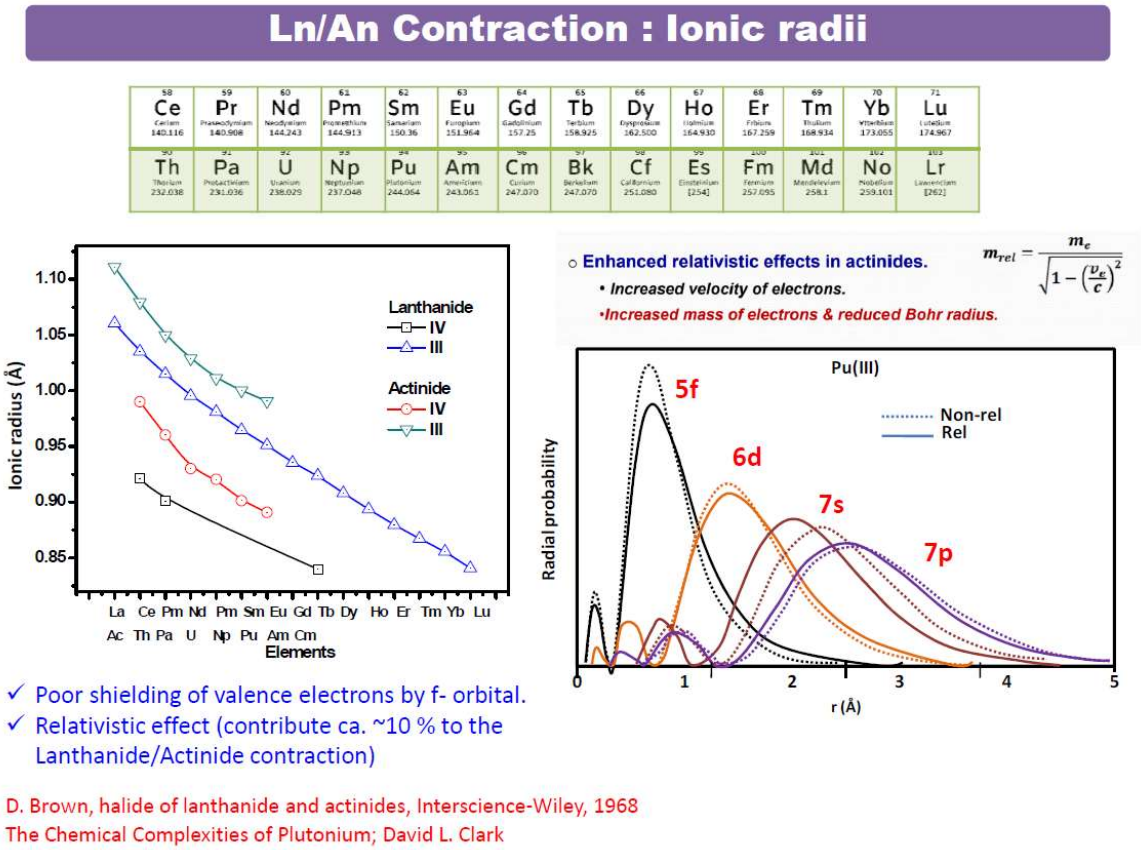
What is disproportionation? This disproportionation is nothing but you start with the one oxidation state, let us say five and that will result in two oxidation states that are +(VI) and +(IV). It is the splitting of one oxidation state into one higher and one lower oxidation state that is very common for the pentavalent ion. As you can see uranium, neptunium, and plutonium all undergo disproportionation, and if you see the equilibrium constant that is very very high for uranium compared to neptunium that again suggests that Np(V) is more stable compared to U(V) and when they disproportionate what they are forming is a lower

oxidation state that is U(IV), and U(VI). Similarly, when you talk about the neptunium then you talk about the neptunium that is NpO_2^+ it will take up 4 protons, so form $Np^{4+}$and NpO_2^{2+}along with $2H_2O$ as given below.

$$NpO_2^+ + 4H^+ \leftrightarrow Np^{4+} + NpO_2^{2+}$$

So, neptunium again starts from Np(V) going to Np (IV) and Np (VI).

This is disproportionation that is mainly happening for the pentavalent but there are other ions also such as this you can see the two oxidation states are combining to give two new oxidation states. This is very common in the actinides that disproportionation reactions that are there for the actinides.



So, now with the knowledge of the exact spherical or linear ion in the actinides and their oxidation states let us talk about how the sizes of these ions vary. As I told you when you talk about +2 to +4, they are mainly spherical, and when you talk about +5, and +6

they are mainly a linear ion. so here we have seen the ionic radii of the actinides as well as lanthanide ions in +3 and + 4 (oxidation states).

I have not shown for the +5 because they are not spherical, they are linear compounds. So, we see that there is a steady decrease whether we talk about the lanthanides or talk about the actinides. There is a steady decrease in the ionic radii of this with the atomic number, because when we talk about the lanthanides the 4f or in the case of actinides this orbital (4f or 5f), they contribute to a very poor shielding and because of the poor shielding whatever electrons we are adding when we are going from here to here (top to bottom) they are feeling more effective charge and because of this there is a contraction and this is linearly decreasing and why this charge the ionic size is different from lanthanide to actinide we are going from 4f here to 5f so the size is on the higher side. Again, in the tetravalent also you can see there is a steady decrease in the size because of the contraction. So, this is lanthanide or actinide contraction that happens because of the poor shielding of the valence electrons by f-orbitals.

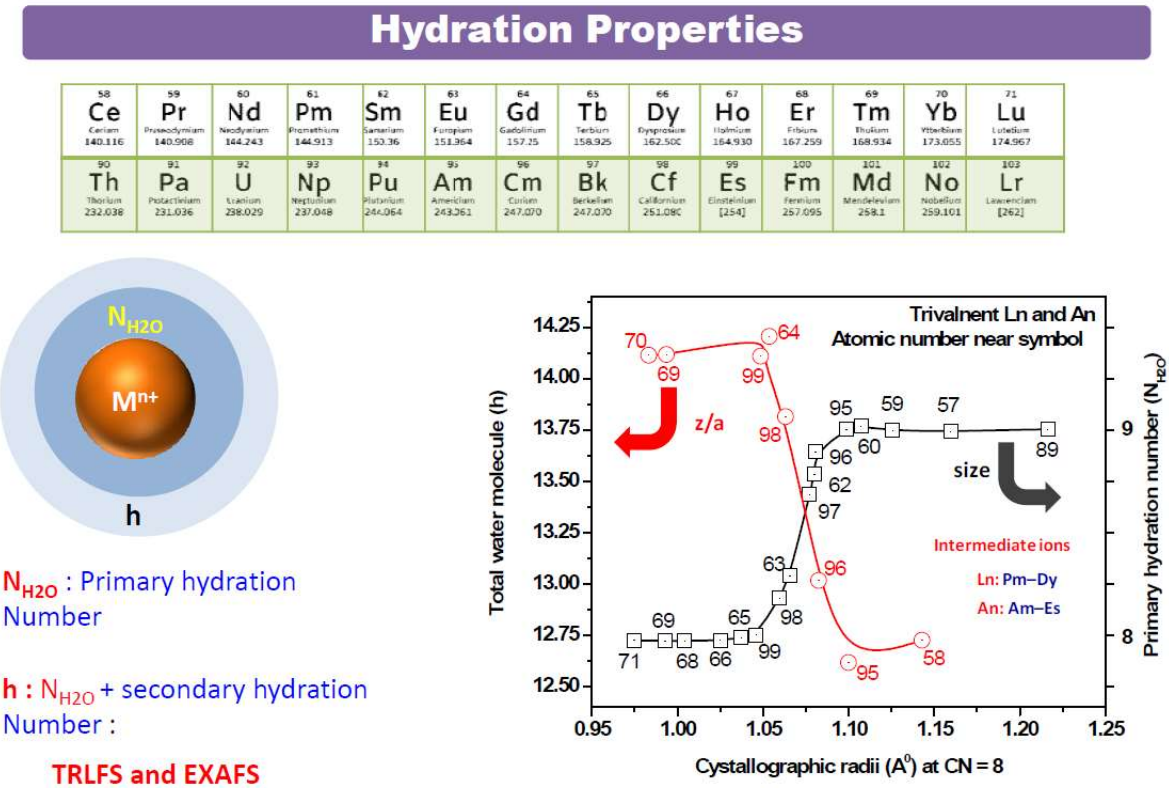
One more very interesting effect that is very important when we talk about heavier atoms is called the relativistic effect.What the effect is when you are in the zone of this high atomic number that is actinium,thorium, protactinium such a very high atomic number what will happen there we have nuclei and the electrons revolve around them.So, when you are increasing this atomic number, the electrons feel more and more pulled fromthe nucleus and its speed keeps on increasing.When you go through a very high atomic number such as in the lanthanides or actinide this attraction (between electron and nucleus)is so much that the speed goes close to the speed of light and when the speed goes too close to the speed of light there is something that is called the relativistic mass that is different from the rest mass (of the electron) and if you compare them where the speed of the electron is ‘v’ is goingclose to the speed of lighti.e. ‘c’ your relativistic mass of the electron keeps on increasing and your relativisticmass and your Bohr radius are inversely proportional.

when the mass is increasing the Bohr radius is contracting and this effect is very much prominent for s and p orbitals.so you can say that s and p orbitals will try to contract

but when we talk about the othertwo that d and f feel the opposite effect, why, because since s (orbital) is getting contractedand p(orbital) is getting contracted now the shielding of nucleus or the shielding of nuclear chargefor the outer electrons are very high so they contract and they shield the outer electronbecause of that d and f do not feel that much amount of attraction from the nucleus andinstead of getting contracted they expand.

This is something called a direct relativistic effect (contraction of s, p orbital) and this is something we say like an indirect (expansion of d, f orbital)relativistic effect the same thing you can see in the figure that happened.Let us see here.We are going to talk about the s and p. If you see if I am considering the relativistic domain and non-relativistic domain in the non-relativistic domain the orbital is here (dotted lines)but the moment we apply this relativistic correction the orbital shifted (solid lines).Then you can see the p orbital this is non-relativistic and this is relativistic.

So, you can say there is a shift towards the nucleus but what about the f and d?The non-relativistic is this side where the relativistic is shifted towards the right so there is a destabilization of d and f whereas there is a stabilization of s and p. So, because of this relativistic effect the contraction of the lanthanide and actinide occurs and almost 10 to 15 percent of the lanthanide and actinide contraction can be attributedto this relativistic effect.So, when we talk about these linear ions. I will not talk about this contractionin size because the linear ions that arePenta- and hexavalent, they are existingas linear ions.So, this is called hexavalent and similarly, I can write for pentavalent also.There the concept of this reduction in the ionic radii we are not going to discussbecause they are linear, they are not spherical and this concept is mainly we are discussing about the spherical ion.



CHAPTER 23: Actinides In Solution: Complexation And Kinetics
Gregory R. Choppin And Mark P. Jensen

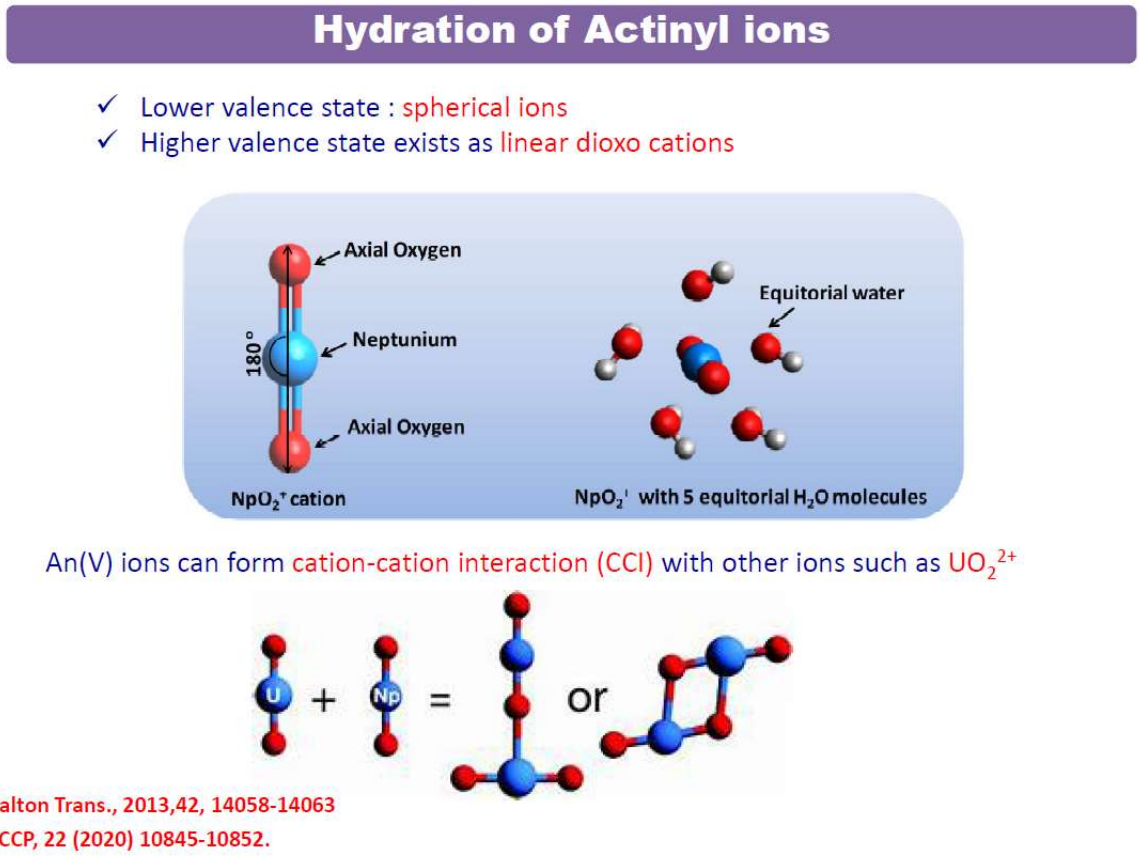
So, the first thing that can happen when you have a metal ion is you know about this size you know about the radius and you put them into the water. What will happen? They will try to hydrate themselves. What can happen if a metal ion you put into water there can be a primary hydration layer just on the metal that we have given as N_H_2O and it can have total hydration which includes both the primary and the secondary (hydration layer) that I have given the name H, that is primary plus secondary. So, the moment you put there isa hydration structure around this metal ion. Let us talk about the trivalent metal ions and what are the hydration structure aroundthe trivalent metal ion.

We can determine this hydration structure obviously because we need to know how many are in the primary sphere and we want to know how many are there in the secondary sphere if we can get information about the total, we can get secondary just by subtracting the primary one from the total. so there are two techniques generally people use to get information about the primary hydration sphere that is fluorescence and EXAFS whereas

to get information about the total you are mainly relying on the electrophoretic mobility kind of experiments in which we measure some kind of diffusion which will tell about the overall radius of the structure and since we know about the radius of this we will try to reduce that what is the total hydration and from this total hydration we subtract primary hydration that we can directly get from these techniques (fluorescence or EXAFS) and we can get the value of the secondary hydration number. so now how these hydration numbers are changing for the trivalent metal ion?So, if you see the trivalent metal ion and you start from this end (right side) this is shown here the initial hydration level shows almost 9 water molecules but the moment you go from left to right (Note: it is from right to left, black curve) what you see there is a decrease and start from 9 and get settled down to 8. Why there is a change from 9 to 8? We are at this position obviously as shown in the previous slide so since the sizes are large, they can accommodate so the size is largerand you can accommodate almost 9 but the moment you move like this your size keeps on reducing.

So, now because of the steric factor accommodating 9 water molecules is very difficult so theysettle down with 8 and a very similar case happens with the actinides alSo, and this transitionwhen you see this particular area that happens for lanthanides at promethium and dysprosium whereas for actinides it happens at americium to einsteinium.Why this smooth transition?Because at this particular place whatever metal ions are coming such as americium, here theycan have both some of them can have 9 H_2O some of them can have 8 H_2O so the hydration is therecan have 9 or 8 so they have this kind of mixture and because of that they follow thisline.What about secondary hydration?If you see the secondary hydration (red line) this is just the reverse although the primary is decreasing from 9 to 8 the secondary when you are going from cerium to terbium keeps on increasingwhy so because as we are reducing the size but we are not reducing the charge everyoneis trivalent so the z by r ratio or you can say the ionic potential keeps on increasing andalthough because of their particular size they cannot accommodate more water into theprimary sphere but because of their electrostatic field that can extend they can now accommodatemore water molecule into the secondary sphere if you talk of the secondary sphere and theytotal is obviously on the larger side so here comes the role of ionic potential that isthe surface ionic potential and this happens because of the again when you talk about

thetetravalence in tetravalent such as thorium we are having generally 10 to 11 water molecules.



What about pentavalent? In the case of pentavalent again, as I told you a little bit special when you talk about pentavalent and hexavalent because pentavalent does exist as a linear action that I have shownhere and the two positions that we say the axial is already occupied orare already blocked by the oxygen and you are only left in the equatorial plane.When we talk about this then the chances of water coming into the plane of the neptuniumare restricted in the equatorial plane only and generally five to six water moleculesare present in the actinide and you talk about the pentavalent actinide orthe hexavalent actinide.

One very interesting aspect that is very peculiar to the, basically to pentavalent ions is cation-cation interaction. When the concentration of these actinides is very low then obviously, they exist as a hydrated ion but suppose, you have a medium in which you have both, Np(V) and U(VI) Suppose you are having both, so U(VI) that is UO_2^{2+} and

neptunium that is NpO_2^+ both are linear cations. So, when they are present together the chances are there that these cations can interact with each other, the mode in which they interact is called T-shape and one is called diamond and these kinds of shapes are very very common in the solution. Why the interaction is taking place? Why such interaction is there? To understand that you can think of the concept of residual charges. What are residual charges? Although I have shown you that the pentavalent actinides that we write as AnO_2^+ we say they are pentavalent but since they have oxygens here oxygens donate part of their electrondensity to these actinides.

It so happens that if you see the charges on the actinide, they are not exactly pentaor hexavalent, they are not exactly five or six.What happens that if you talk about neptunium let us say NpO_2^+ and if you charge onneptunium exactly it will be around 2.2 whereas if you see about the uraniumUO_2^{2+} and you try to see the charge on uranium then they are around +3.3.so these charges are different than whatever we see whether they are pentavalent orhexavalent but which is the actual charges it is +2.2 for pentavalent and +3.3for hexavalent ion and now since the charges are different this again has some partialnegative charge and this partial negative charge can interact with the positive chargeof the uranium which is +3.3 and they can make this kind of complex which is known as cation-cationcomplex and it is very very unique properties of the actinide that cation-cation formationwith not with uranium only. you can have another metal ion, for example, you can have thoriumand as the charge increases the interaction gets stronger and stronger.So, with this, I want to end this lecture and we will discuss the other concept in the next upcoming lectures.

Thank you very much.

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