Course Name: Nuclear and Radiochemistry
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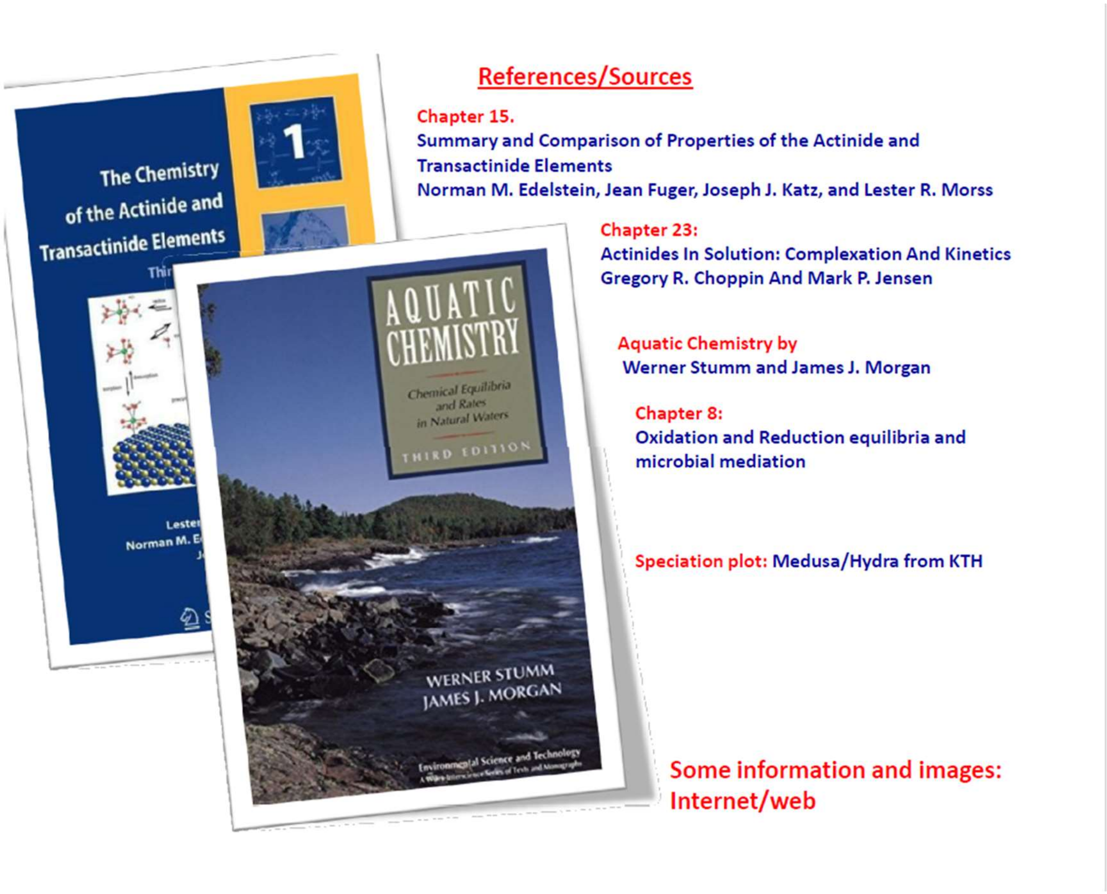
Institute Name: Homi Bhabha National Institute
Week - 09
Lecture - 45

Helloeveryone, Welcome back to the series of lectures on actinide chemistry, we have discussed a bit about the aquatic chemistry of the f-block elements in the last lecture.So, today we will try to learn something about the pH-pE diagram, and before going to the presentation, I just want to have a mention of the references that, I used for preparation of this presentation.



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

Aquatic Chemistry by
Werner Stumm and James J. Morgan

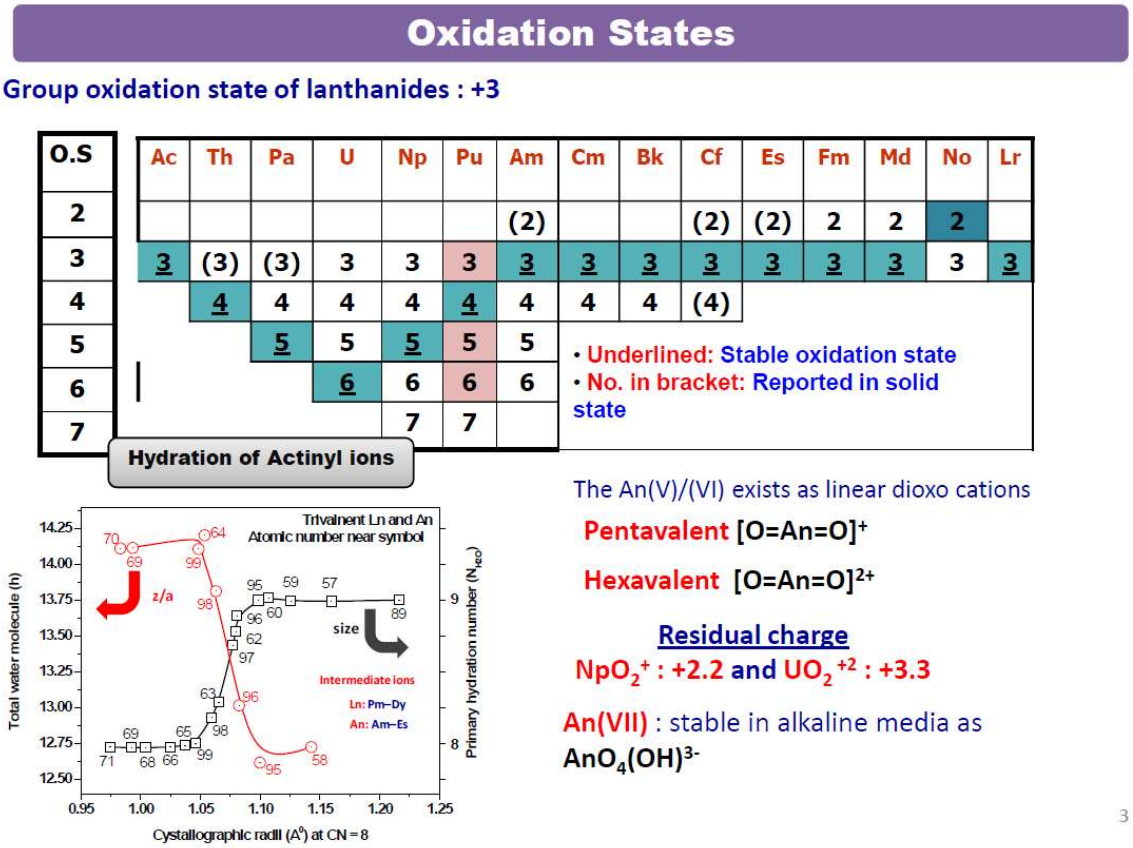
Chapter 8:
Oxidation and Reduction equilibria and microbial mediation

Speciation plot: Medusa/Hydra from KTH

Some information and images: Internet/web

The first is the chemistry of the actinide and transactinide elements, andthe second is the aquatic chemistry. I have also used some of the programs for the speciation plot that I have taken from the KTH, known as Medusa or Hydra. Some of the images are taken from the internet or the web as per convenience for better explanations, I have modified them. So, these are the few references that I have mainly

used. Besides that, whatever references I have used I have tried to quote them on the respectiveslides.Before going to the next lecture, I would just like to mention whatever we have read in the previous lecture, and a recap of that.



Oxidation States

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

Hydration of Actinyl ions

The An(V)/(VI) exists as linear dioxo cations

Pentavalent $[O=An=O]^+$

Hexavalent $[O=An=O]^{2+}$

Residual charge

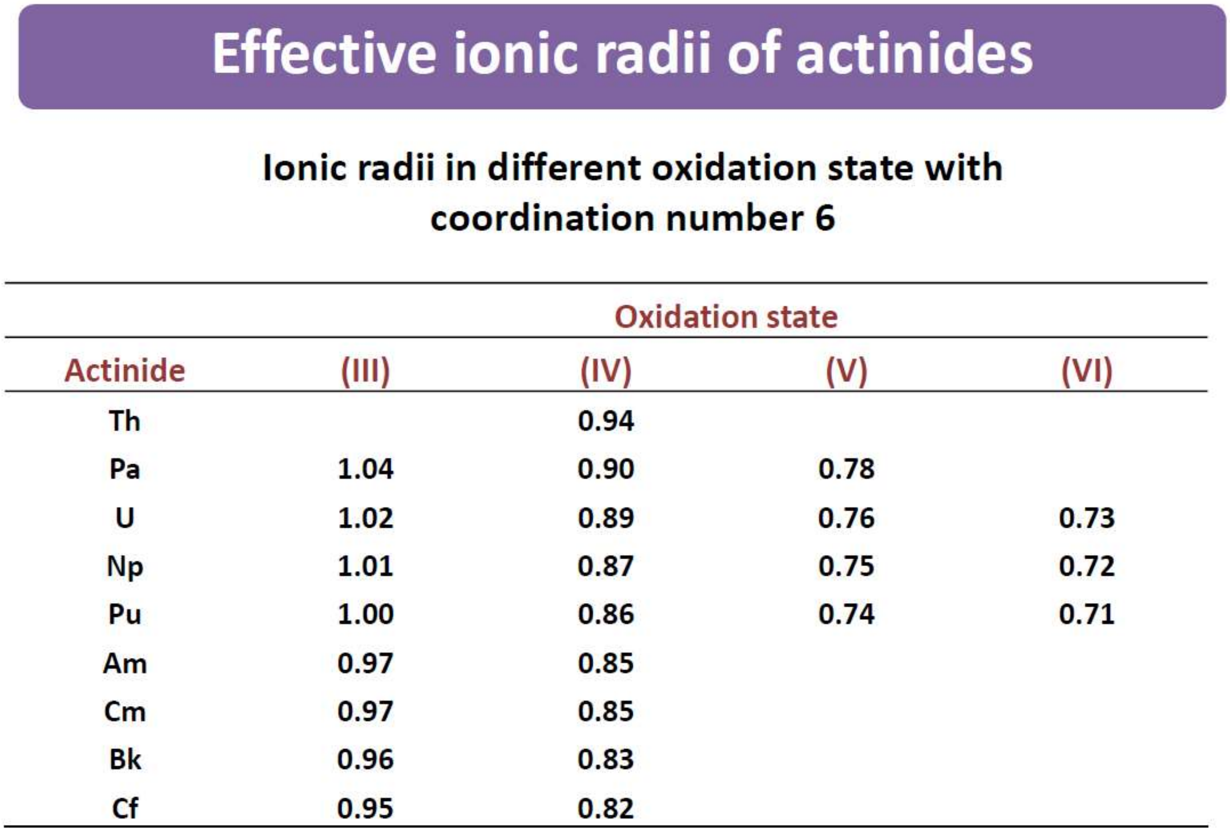
NpO_2^+ : +2.2 and UO_2^{+2} : +3.3

An(VII) : stable in alkaline media as $AnO_4(OH)^{3-}$

So,there we have started with the electronic configuration, and we have seen that the group oxidation state of lanthanides is +3 whereas, when we talk about the actinides, they can have a variable oxidation states starting from +2 to +7.So, there we have seen that this kind of variation in the oxidation state of the actinides is mainly coming because there the filling of electrons in the 5f orbital which has close energetic proximity with the 6d, and 7sorbital, and because of that, we are getting such variation in the oxidation states of actinides.

We have also learned about the different ions that are possible in the actinide, and we have seen that the divalent, trivalent, and tetravalent ions are spherical ions but when we talk about the other valency that is pentavalent ion and the hexavalent ion, they are no more spherical but are linear ion, called as actinyl ions. If I must draw it is like, suppose you must take uranium it is like uranium which is called trans-dioxo compounds. So, here we can see that the formula charge is 2+ so you can see the total charge is 2+ whereas, we say it is like hexavalent so uranium 6+ but if you start looking into the chemical properties of this uraniumactinyl ions, you find that they are neither behaving like pure 2 + nor 6 +butsomewhere in between. So, lots of groups have worked on this, and finally, they have concluded that the bonding or the chemical properties of this kind of ions or this kind of actinyl ions can be explained by linear dioxo structure with +2.2 units charge on actinide in the case of pentavalent, and+3.3 units charge in the case of hexavalent ions.

We have also tried to see, what the hydration structure of different actinides in the water, and here we have just discussed that the trivalent starts with CN around 9 water molecules andcan reach up to 8 water molecules, and there is a transition from 9 water molecules to 8 water molecules so it is a transition zone. This is about the first hydration sphere, and we have also seen in the second hydration sphere that the total hydration number is increasing in the reverse order, and we have tried to rationalize this by size, and total surface charge density. So, with this basic background, I would like to go to the next slide that we are going to discuss.



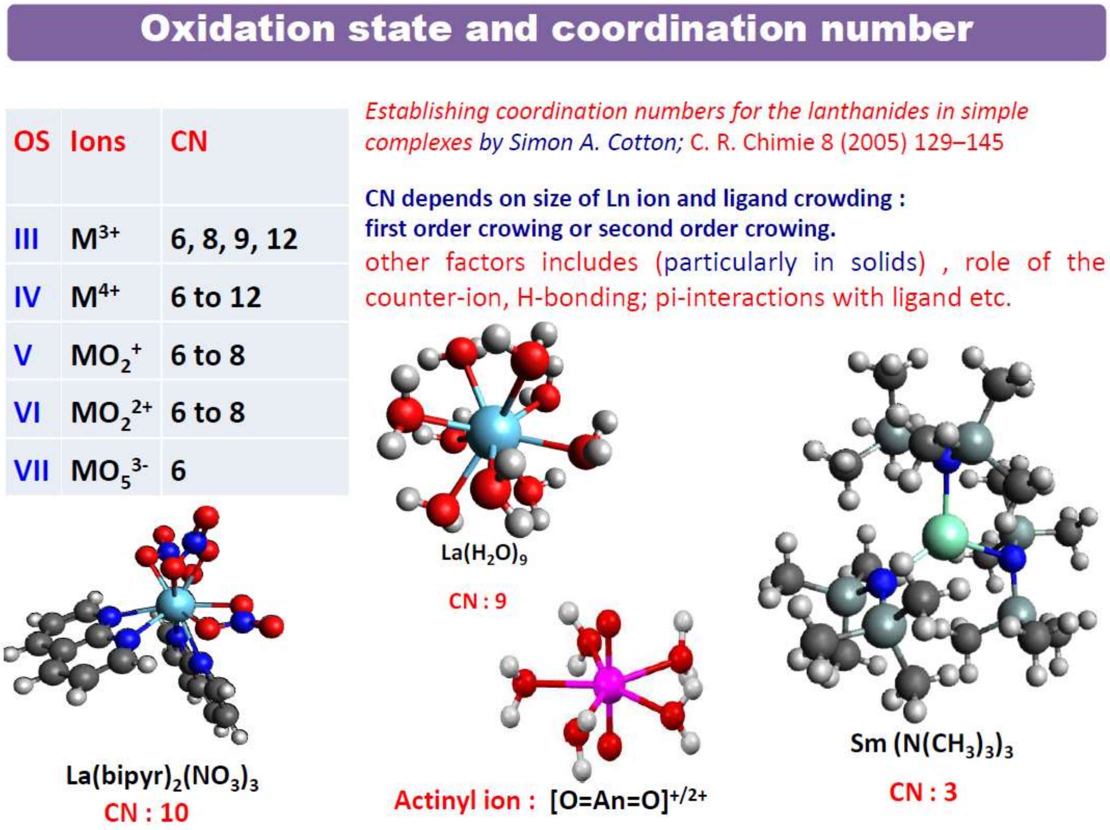
Effective ionic radii of actinides

Ionic radii in different oxidation state with coordination number 6

	Oxidation state			
Actinide	**(III)**	**(IV)**	**(V)**	**(VI)**
Th		0.94		
Pa	1.04	0.90	0.78	
U	1.02	0.89	0.76	0.73
Np	1.01	0.87	0.75	0.72
Pu	1.00	0.86	0.74	0.71
Am	0.97	0.85		
Cm	0.97	0.85		
Bk	0.96	0.83		
Cf	0.95	0.82		

Yeah, so what are the different ionic radii? We have discussed the lanthanide and actinide contractions, and here I have given you some of the values for the ionic radii in the different oxidation statesof lanthanides or actinides.

This we have already discussed in the lanthanide and actinide contractions. We have shown you some graphs for that. So, I am not going into much detail about this. This is just for your reference that some of the values are given, and as you can see, they are having a decreasing trend because of the lanthanide, and actinide contractions or actinide contractions in the respective actinides.



Oxidation state and coordination number

OS	Ions	CN
III	M^{3+}	6, 8, 9, 12
IV	M^{4+}	6 to 12
V	MO_2^{+}	6 to 8
VI	MO_2^{2+}	6 to 8
VII	MO_5^{3-}	6

Establishing coordination numbers for the lanthanides in simple complexes by Simon A. Cotton; C. R. Chimie 8 (2005) 129–145

CN depends on size of Ln ion and ligand crowding :
first order crowing or second order crowing.

other factors includes (particularly in solids) , role of the counter-ion, H-bonding; pi-interactions with ligand etc.

$La(H_2O)_9$
CN : 9

$La(bipyr)_2(NO_3)_3$
CN : 10

Actinyl ion : $[O=An=O]^{+/2+}$

$Sm(N(CH_3)_3)_3$
CN : 3

So, once you have water, you add actinide salts into the water medium what will happen? is that your water will be there in the primary coordination sphere.

So, now the question arises what is the coordination number of a given oxidation state on lanthanide or actinide? So, here in general the trivalent prefers +9, the tetravalent prefers between 6 to 12 but generally 10 you can say, and the pentavalent as I have shown you are not spherical ions but are linear ions. So, they have very different coordination numbers from 6 to 8. Hexavalent is again 6 to 8, and heptavalent actinides which specifically exist in the alkaline medium only have a coordination number of around 6. But this is a very rough estimate. So, I can give some examples where the ions that are in the trivalent state can have coordination numbersthat are very different from whatever I have written.

So, for example in general, I have shown you this. This is coordination number 9. This is the aqua molecule. You can see 8, and 9 water molecules surrounding the lanthanum ion. But there are cases in which the coordination number goes as low as 3.

Why? Because in general, the coordination number depends on two factors. One is the size of your lanthanide ion. The second is ligand crowding or when I say ligand crowding two very important factors are called first-order crowding, and second-order crowding. What do I mean by this first-order crowding or second-order crowding? let us talk about first-order crowding. So, when your ligands are very small molecules like water molecules or nitrate ions. When your ligands have a small molecule, and they are directly coordinating, the second sphere has very small molecules/groups like there you have an H atom for water and N for nitrates. So, in these cases, you can say the primary crowding is because of the oxygen but there is no or very low secondary crowding. But what happens when your ligand structure has some kind of moiety such as N with some kind of long chain alkyl groups or maybe some kind of phenyl group? So, besides the first coordinating atom the second group is too big that it causes some sort of steric hindrance or some sort of crowding, and because of this kind of crowding the coordination number decreases drastically.

So, here in this example as you can see the coordination number has decreased to 3. So, such a decrease is mainly coming because of the secondary crowding. I have also shown you an example where the coordination number is again increased to 10. So, saying the coordination number of almost 9 is okay for the solution chemistry but when we talk about the overall compounds or the other compounds in the solid state then the coordination number varies to a very large extent.

For example, let us talk about the thorium. Thorium can have coordination numbers from 4 to as high as 15. Such a huge range of coordination numbers is possible in the case of thorium compared to the other metal ions. In general, the trivalent ions are 9 coordinated, the tetravalent has 10 to 12 coordination. What about the pentavalent, and hexavalent? Here I have shown you some examples of the pentavalent ion.

As you know, the pentavalent/hexavalent has a dioxo-linear structure. So, here you can easily see that the axial positions are already occupied by oxygens. So, now the ligand has only the choice to come into the equatorial plane, and the equatorial plane can have at most 5 to 6 coordination numbers. For example, in the aqua complex, you can see 5 aqua ions coming in the equatorial plane. So, the total coordination number is 5 from equatorial (sometimes maybe 6) and 2 that you have in axial position giving a total of 7 to 8 coordination numbers.

So, in general, the hexavalent ions have a 7 to 8 coordination number. Again, the same is true for the pentavalent also because this I have shown for uranium but suppose you have a case of neptunium again which is a linear ion with a plus charge, and here again we can have 5 to 6 water molecules in the primary coordination sphere or you can say in the equatorial plane giving a total coordination number of around 7 to 8. So, this is all about the coordination numbers of the different oxidation states of the actinides. So, with the knowledge of hydration, and the coordination number let us try to understand, what is the thermodynamics of hydration.

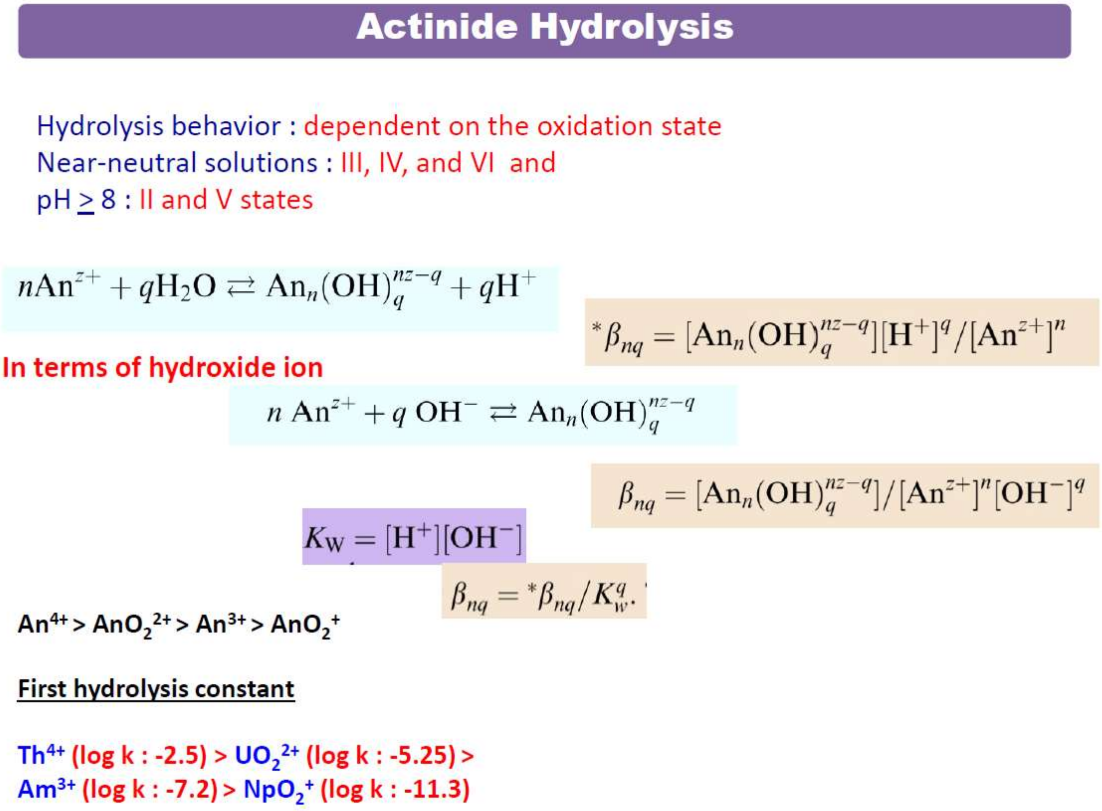
So, as we have seen when you put any gaseous ion or ion in the gaseous state to the aqueous system there is stabilization or the overall ΔG is becoming more, and more negative. We have also seen that when you have an ion there is a hydration sphere one is called the primary, and the other is the secondary hydration sphere, and we have also talked about the number of water molecules in the primary, and secondary hydration spheres.

So, when the metal ions in the gaseous state are moving into the aqueous medium. What will happen there is the water molecule will try to arrange itself around this metal ion, and there is some interaction between the water molecule and metal ion, and because of that interaction there is a release of energy or you can say the process is exothermic. So, overall ΔH is becoming negative but at the same time when you see the entropy factor, we know that when you talk about the ΔG there are two factors one is ΔH, and the other is entropy. Two sectors control the total ΔG value one is ΔH which shows that when there is an interaction between the water molecules or the solvent molecule with the metal ion there is a huge stabilization or exothermicity in the ΔH but what about the entropy factor? Entropy is basically as we know it about randomness. So, if the randomness is increasing entropy is increasing but if the randomness is getting decreased the entropy will be decreased, and here you can see when the water molecule is in the bulk, they are freer or have more entropy but the moment these water molecules are coming close to the metal ions they are having some sort of structure.

So, now the entropy of the system is getting decreased. So, in a way, I can say with the total ΔG that we want to derive for the hydration of these aqueous ions the ΔH is favoring whereas the ΔS is not favoring but the amount of ΔS that is there if you see from the table keep in mind that these values are in kilojoule for the ΔH, and for ΔS it is in joule. So, I have written specifically in joule because that is the unit we generally prefer. So, if you use the ΔH value, they are of the order of 3000 to 3500 whereas if you see the ΔS it is between 300 to you can say 400. So, when you take the total value that is T ΔS, and subtract it from ΔH to get ΔG, we found that the total contribution of entropy term to this ΔG value is not more than 3 to 5 %.

So, this stabilization is mainly coming from the ΔH so it is entropically not favored but enthalpy is very favored. So, I have given you some plots here I have plotted all three quantities that is ΔS ΔH, and ΔG. You can see the ΔH keeps on decreasing or I can say enthalpy is more favorable because we are getting more, and more negative values as we are moving, and the ΔS is also following almost the same trend, and when we take the difference according to this equation we are getting ΔG which is again a negative but why this kind of trend because when we talk about the ΔH suppose we take ΔH first as we move in this series what will be there there is a decrease in the size or you can say the total increase in the z by r ratio. So, when the z by r ratio or the ionic potential is getting increased there is more and stronger interaction between the metal ion and water molecule. This interaction is becoming stronger, and stronger, and because of that the energy released is more, and more so that is why we are getting more, and more negative energy.

Similarly when there is more interaction suppose there is low interaction at this so the only structure of the water molecule is there in the primary sphere, and the secondary is not very much in the primary sphere but the moment you are getting to a very higher potential a very high ionic potential there is some sort of structuring in the secondary sphere also, and because of that you can see there is a constant decrease in the entropy term then again we will just take care of entropy, and enthalpy find out the ΔG value, and what we found that the ΔG values are again very much negative in this cases which is giving the stabilization to the ions in the aquatic media.



Actinide Hydrolysis

Hydrolysis behavior : dependent on the oxidation state
Near-neutral solutions : III, IV, and VI and
pH $\geq$ 8 : II and V states

$$n\mathrm{An}^{z+} + q\mathrm{H_2O} \rightleftarrows \mathrm{An}_n(\mathrm{OH})_q^{nz-q} + q\mathrm{H}^+$$

$$^*\beta_{nq} = [\mathrm{An}_n(\mathrm{OH})_q^{nz-q}][\mathrm{H}^+]^q/[\mathrm{An}^{z+}]^n$$

In terms of hydroxide ion

$$n\ \mathrm{An}^{z+} + q\ \mathrm{OH}^- \rightleftarrows \mathrm{An}_n(\mathrm{OH})_q^{nz-q}$$

$$\beta_{nq} = [\mathrm{An}_n(\mathrm{OH})_q^{nz-q}]/[\mathrm{An}^{z+}]^n[\mathrm{OH}^-]^q$$

$$K_\mathrm{W} = [\mathrm{H}^+][\mathrm{OH}^-]$$

$$\beta_{nq} = {}^*\beta_{nq}/K_w^q.$$

$An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^+$

First hydrolysis constant

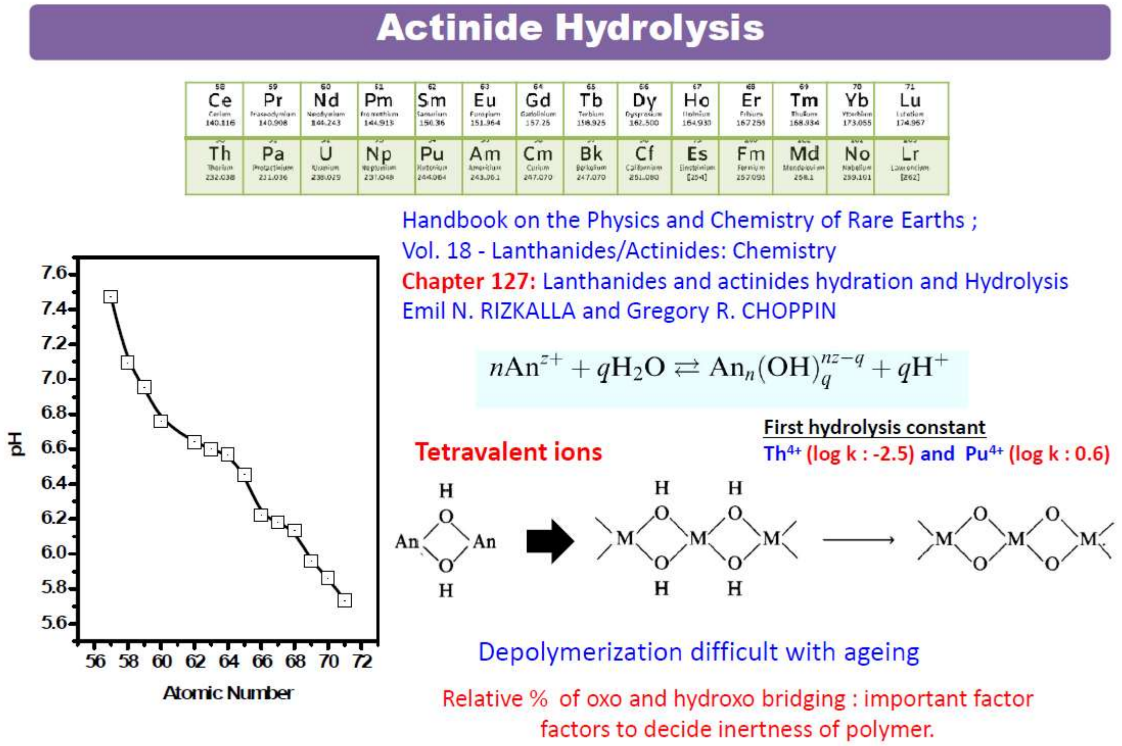
Th^{4+} (log k : -2.5) > UO_2^{2+} (log k : -5.25) >
Am^{3+} (log k : -7.2) > NpO_2^+ (log k : -11.3)

Once you have this ion in aquatic media, they are stabilized in some form what else can happen to them? The next thing that can happen to them is the hydrolysis. So, when you have ions in the media they can act as surrounded by some water molecule that is the x number of water molecules so the next thing that can be there in the hydrolysis because this metal ion tends to attract the oxygen from the H_2O, and slowly so happens that this kind of hydrolysis equilibria can establish into the aquatic media, and as I have shown you that we are having different kind of ions that is spherical, and linear so their hydrolysis behavior is very much different from each other, and if you assume this kind of equilibria for the hydrolysis you can always write hydrolysis equations, and in second case suppose you are adding to some of the alkalis to the media then obviously you can write this kind of equilibria, and these two equilibria are related with each other with the ionic product of water, and you can get this.

There are very simple mathematical equations that you can always write, and you can get information about different kinds of equilibria that are there but the most important thing that I want to discuss here is at what point hydrolysis will occur, and which metal ions which are more prone to the hydrolysis.

In general, as they have written it is dependent on the oxidation state of the metal ion, and when we see the oxidation state the trend I have given is that it is most prominent for the tetravalent followed by hexavalent, trivalent, and pentavalent, and keep in mind that when I say hexavalent I assume a charge of 3.3, and it is 3 so you can see there is a good decrease you start with 4 +, and then you have a charge of 3.3 then 3, and then 2.2 so it is perfectly going with the charge of the central metal ion.

The second thing is the oxidation state which has a different structure they are called actinyls generally I have shown you that the actinides with the pentavalent are linear so their hydrolysis is very very poor again because of the charge. If you see the value wise if you see the thorium hydrolysis constant concerning others, I have given some of the values here if you see the thorium logk value for this the hydrolysis reaction is around -2.5 whereas for uranium it is -5.25 these are the log k values so if you try to write them in the form of k this will be like 10 to the power -2.5 and 10 to the power -5.25. What I mean by that is if you just take the ratio you can see the thorium tendency of thorium to get hydrolyzed is almost 500 times more than that of the uranyl ion, and when you talk about uranium to americium it is again almost 100 times than uranium, and this is very weak as you can see it is going from -7 to -11 so it is almost 1000 times lower so this hydrolysis is taking place depending on the ions. So, when you have ions, and they get hydrolyzed how their hydrolysis tendency is varying with the atomic number we can say in the series in the lanthanide series.



Actinide Hydrolysis

Handbook on the Physics and Chemistry of Rare Earths ;
Vol. 18 - Lanthanides/Actinides: Chemistry
Chapter 127: Lanthanides and actinides hydration and Hydrolysis
Emil N. RIZKALLA and Gregory R. CHOPPIN

$$n\mathrm{An}^{z+} + q\mathrm{H_2O} \rightleftarrows \mathrm{An}_n(\mathrm{OH})_q^{nz-q} + q\mathrm{H}^+$$

Tetravalent ions

First hydrolysis constant
Th^{4+} (log k : -2.5) and Pu^{4+} (log k : 0.6)

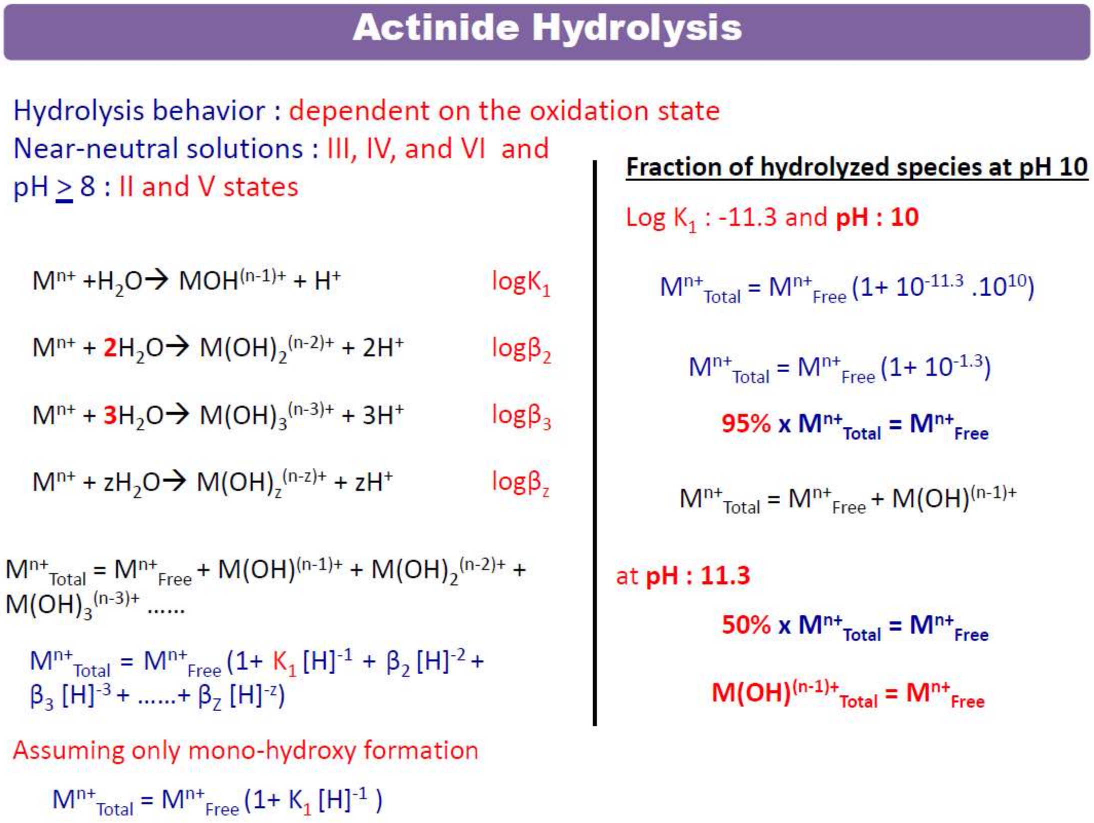
Depolymerization difficult with ageing

Relative % of oxo and hydroxo bridging : important factor
factors to decide inertness of polymer.

So here in this particular graph, I have shown you the onset of precipitation concerning the atomic number. Here you can see as we are moving in the chain from the lanthanide to lutetium the pH at which the hydrolysis will occur is decreasing what does it mean that the ionic potential as we move the size is decreasing so the ionic potential is increasing now the ionic potential is becoming so higher that even at low pH you can get the hydrolysis. So, this is for the trivalent, I have shown you the trivalent but what about the tetravalent I have shown you in the previous slide that tetravalent is almost 500 times more prone to hydrolysis compared to the trivalent. So when you see the tetravalent, and you compare the thorium with another tetravalent that is plutonium if you see the hydrolysis constant these are again an order of magnitude higher for the plutonium compared to the thorium.

This is again you can explain because as we are moving from here to here there is a decrease in size, and since the charge is almost the same the ionic potential is on the very high side, and then they form hydrolysis very rapidly compared to the thorium. So, when we talk about the hydrolysis for the normal trivalent, they are or maybe you can say pentavalent, and hexavalent, pentavalent mainly they are forming a kind of complex which we say is the MOH, M kind of complex which is you can say mononuclear or only with one metal ion but when we talk about the tetravalent ion their hydrolysis is we say it is polynuclear. Why polynuclear? Because it so happens many times that more than one metal ions are there in the hydrolysis. When you just add some alkali, they will just make some mononuclear complex or mono hydroxy complex, and the moment you add a little more alkali or the pH goes a little on the higher side, they come together, all the molecules come together with this basic unit, and they try to make some amorphous hydroxy phases. for tetravalent this kind of phenomenon is very very prone, and I must tell you that if you see an example, if you see let us assume that this n is 1 here, and you are having some tetravalent, and if I say that the number of protons released per metal ion so, what I am trying to say that, if you react with this, and there is one proton release so per metal ion one proton is released the moment this goes to 2 or beyond 2 you can say the number of protons released goes to beyond 2 the hydrolysis is so fast or so rapid that the number of units of thorium that come together is more than 100 or you can say the cluster is having more than 100 thorium atoms in this hydrolyzed products.

So, the basic unit of this is -MOH- they start with this in the very freshly prepared, and when they are freshly prepared as I have shown you these equilibria when they are very much freshly prepared with these equilibria one can easily understand that, if you increase this acidity, you can get back so when they are freshly prepared, and you are trying to increase the acidity of the medium. we can dissolve them but what if they are getting aged with time? they make this kind of structure, and if you put it even for a longer time they will make this kind of structure (see slides), so you can see some of the hydroxy groups are now removed, and there are oxy groups, oxolation is happening so the tendency of formation of this is very very slow but if it has formed its solubility just by increasing the acid of the media is very very poor so this depolymerization this phenomenon is a polymerization so when I say depolymerization, we are trying to get back this to our metal ion so this depolymerization is becoming very very difficult when we are talking about the aging, and this depolymerization tendency is basically dependent on the percentage of oxo, and hydroxy bridging. if the percentage of oxo bridging is very high then this depolymerization is very very difficult. Whereas, if the percentage of hydroxy bridging is high, we can have still some sort of backward reaction or you can say depolymerization with this. So now the question arises okay, we know something about hydrolysis.



Actinide Hydrolysis

Hydrolysis behavior : dependent on the oxidation state
Near-neutral solutions : III, IV, and VI and
pH $\geq$ 8 : II and V states

$M^{n+} + H_2O \rightarrow MOH^{(n-1)+} + H^+$ logK$_1$

$M^{n+} + 2H_2O \rightarrow M(OH)_2^{(n-2)+} + 2H^+$ logβ_2

$M^{n+} + 3H_2O \rightarrow M(OH)_3^{(n-3)+} + 3H^+$ logβ_3

$M^{n+} + zH_2O \rightarrow M(OH)_z^{(n-z)+} + zH^+$ logβ_z

$M^{n+}_{Total} = M^{n+}_{Free} + M(OH)^{(n-1)+} + M(OH)_2^{(n-2)+} + M(OH)_3^{(n-3)+}$ ……

$M^{n+}_{Total} = M^{n+}_{Free}(1 + K_1 [H]^{-1} + \beta_2 [H]^{-2} + \beta_3 [H]^{-3} + \ldots\ldots + \beta_Z [H]^{-z})$

Assuming only mono-hydroxy formation

$M^{n+}_{Total} = M^{n+}_{Free}(1 + K_1 [H]^{-1})$

Fraction of hydrolyzed species at pH 10

Log K$_1$: -11.3 and **pH : 10**

$M^{n+}_{Total} = M^{n+}_{Free}(1 + 10^{-11.3} .10^{10})$

$M^{n+}_{Total} = M^{n+}_{Free}(1 + 10^{-1.3})$

95% x $M^{n+}_{Total} = M^{n+}_{Free}$

$M^{n+}_{Total} = M^{n+}_{Free} + M(OH)^{(n-1)+}$

at **pH : 11.3**

50% x $M^{n+}_{Total} = M^{n+}_{Free}$

$M(OH)^{(n-1)+}_{Total} = M^{n+}_{Free}$

we know the trend like, the tetravalent has a very high hydrolysis constant compared to the other trivalent or divalent but suppose somebody asked me that can you tell me about that what is the fraction what is the fraction of hydrolyzed species that is formed when I am doing some reaction at a given pH. so how we can calculate this value? so for that, I have given you some scheme. you start with the assumption that yes you are having this kind of equilibrium which is having the certain log k value obviously, and then the other in which I have started from mono hydroxy to dihydroxy to trihydroxy, and finally to z amount of -OH groups (eqs 1-4).

$M^{n+} + H_2O \rightarrow MOH^{(n-1)+} + H^+$ …..1

$M^{n+} + \mathbf{2}H_2O \rightarrow M(OH)_2^{(n-2)+} + 2H^+$ …..2

$M^{n+} + \mathbf{3}H_2O \rightarrow M(OH)_3^{(n-3)+} + 3H^+$ …..3

$M^{n+} + \mathbf{z}H_2O \rightarrow M(OH)_z^{(n-z)+} + zH^+$ …..4

so, when we have this kind of equilibrium we can write the log k value, and I assume that you are familiar with these two terms that is K_1, and β_1, β_2, etc. One is the stepwise constant, and the other is cumulative when I say cumulative what I mean is that this β_2 is nothing but the product of K_1 and K_2. So, these are cumulative so with this knowledge of logβ value, and logK value, how can we arrive at the fraction or the percentage of hydrolyzed species at a given pH for a given metal ion?

So, what we can do? we have this knowledge of logK or logβ for metal ions. we have added some amount of metal ion i.e., total M that whatever we have added now in the system at a given pH or a given condition is present as M_{free} plus different hydrolyzed species of M starting from mono-, di-, hydroxy to other higher hydroxy.

$M^{n+}_{Total} = M^{n+}_{Free} + M(OH)^{(n-1)+} + M(OH)_2^{(n-2)+} + M(OH)_3^{(n-3)+} \ldots$ …..5

Total M is always fixed, and the fractions of hydrolyzed species will keep on changing depending on the system pH.

suppose you can write this total M in terms of this logK or logβ values, and proton. so, what I have done is I have taken the relation between K_1, and β_2. Using this relation, I have tried to write equation 6 in terms of free metal ion, and the proton concentration

$M^{n+}_{Total} = M^{n+}_{Free} (1+ K_1 [H]^{-1} + \beta_2 [H]^{-2} + \beta_3 [H]^{-3} + \ldots\ldots + \beta_Z [H]^{-z})$ …..6

so, if you can write in this manner, we get an equation like this

$M^{n+}_{Total} = M^{n+}_{Free} (1+ K_1 [H]^{-1} + \beta_2 [H]^{-2} + \beta_3 [H]^{-3} + \ldots\ldots + \beta_Z [H]^{-z})$ …..6

So, for simplicity, I have assumed the formation of only mono hydroxy complex so in that kind of condition, the above equation will reduce to

$M^{n+}_{Total} = M^{n+}_{Free} (1+ K_1 [H]^{-1})$ …..7

From this, we will try to find out the fraction of species or the mono hydroxy species that are formed in the different pH conditions. the first thing I tried was to find out the fraction of hydrolyzed species at pH 10 before that I had to give some log k value so here I have assumed a log k1 value of -11.3 for first hydrolysis. So, with this log k1 value of -11.3, what will happen at pH 10? the relation is very simple.

$M^{n+}{}_{Total} = M^{n+}{}_{Free}\,(1+ 10^{-11.3}\,.10^{10})$ …..8

By solving this, we found that at this pH of 10 with the first hydrolysis constant of -11.3, the fraction of free metal ions is more than 95 % so you can say the fraction of hydrolyzed is less than 5 % or close to 5 %.

$M^{n+}{}_{Total} = M^{n+}{}_{Free}\,(1+ 10^{-1.3})$ …..9

$95\% \text{ x } M^{n+}{}_{Total} = M^{n+}{}_{Free}$ …..10

So now, we can find out that at a given pH if the log K values are known, what is the fraction of hydrolyzed species that are present in the solution?

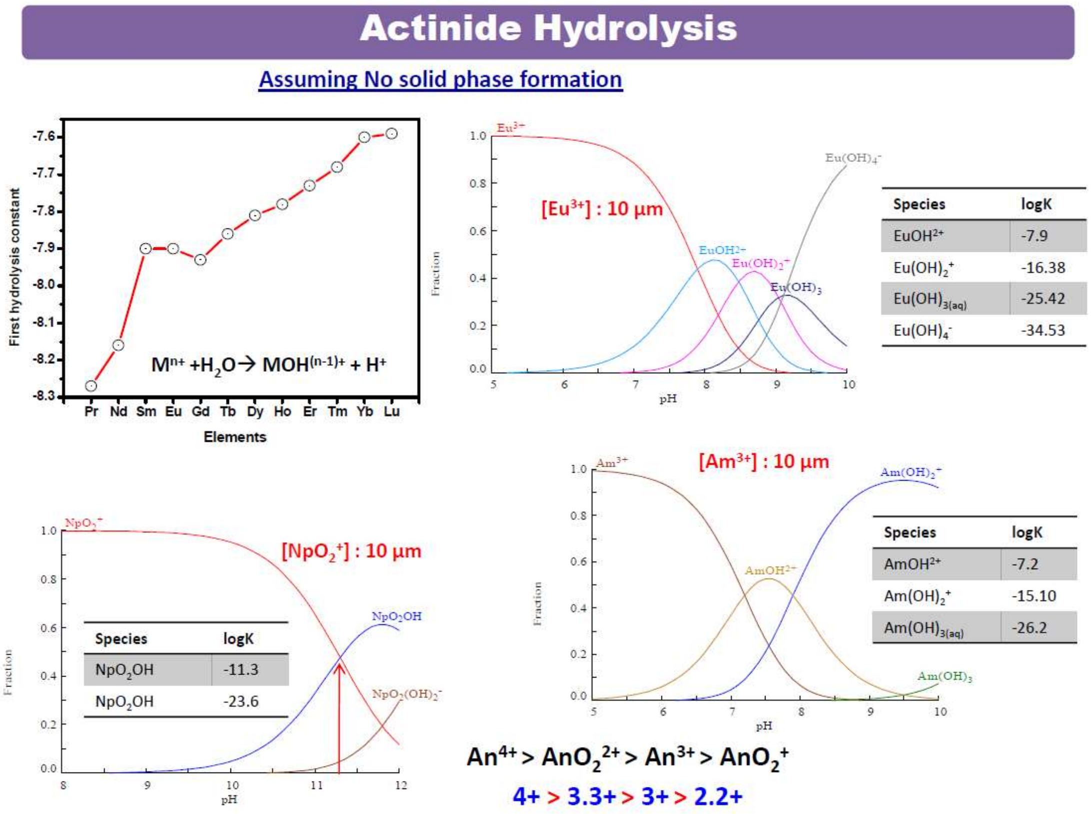
let us increase the pH from pH 10 to pH 11.3, Now we just do the calculations again, and we found that at this particular pH, 50 % of the total metal ions are present as free metal ions. what it means is that since I have assumed the formation of only mono hydroxy species my total metal ion concentration is nothing but the sum of mono hydroxy, and free, what I am saying is that 50 % of the total is acting as a free, so what is rest is also 50 %.

$M^{n+}{}_{Total} = M^{n+}{}_{Free} + M(OH)^{(n-1)+}$ …..11

$50\% \text{ x } M^{n+}{}_{Total} = M^{n+}{}_{Free}$ …..12

$M(OH)^{(n-1)+}{}_{Total} = M^{n+}{}_{Free}$ …..13

Hence, I can say that at this pH both free metal ion and monohydroxy species are almost 50-50 %, and if you look carefully this pH is nothing but just a negative of your log k_1 value. so, what you can say is that if you have information about this logK value, and if you know this simple calculation, you can easily tell that at what a given pH, what kind of species are forming, and where the hydrolysis will start. so, this is the very simple case, I have discussed with the monohydroxy species but obviously, in real systems, we do not have this kind of species and we generally have a combination of mono, di, tri, and in those cases, we must take care of all these equations. all these terms in the equation, and you have to solve it, after solving this what you will get is nothing but a plot in which the x-axis is basically your pH, and the y axis you can plot the fraction of the ion so you can say initially a 100 % is your total or maybe free, and then with the increasing pH there is a decrease, and there is an increase in the hydroxy species of different kinds, these plots are generally known as a speciation diagram or you can say the hydrolysis diagram, where we see that how the hydrolysis of the metal ion is taking place as a function of the pH.



Actinide Hydrolysis

Assuming No solid phase formation

$M^{n+} + H_2O \rightarrow MOH^{(n-1)+} + H^+$

$[Eu^{3+}]$: 10 μm

Species	logK
$EuOH^{2+}$	-7.9
$Eu(OH)_2^+$	-16.38
$Eu(OH)_{3(aq)}$	-25.42
$Eu(OH)_4^-$	-34.53

$[NpO_2^+]$: 10 μm

Species	logK
NpO_2OH	-11.3
NpO_2OH	-23.6

$[Am^{3+}]$: 10 μm

Species	logK
$AmOH^{2+}$	-7.2
$Am(OH)_2^+$	-15.10
$Am(OH)_{3(aq)}$	-26.2

$An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^+$

4+ > 3.3+ > 3+ > 2.2+

I have shown you some of the diagram for the hydrolysis of Europium, Americium, and Neptunium, here I have also shown you what one trend that how this first hydrolysis constant is changing when you are going through the series when you are going through the lanthanide series here again you can see that the first hydrolysis constant keeps on increasing when you are going from the praseodymium to lutetium why this because again here the charge is assumed to be + three only, and when the charge is + three the size is decreasing the z by r ratio is again increasing so they are having more, and more ionic potential, and because of this more, and more ionic potential their tendency to react with the oxide ion with the hydroxide ion is increasing, and you can say there is some change that is basically we called it the gadolinium break kind of things because here if the configuration is becoming f7 that is half field configuration, and because of that there is some perturbation in this curve otherwise you can say this is a monotonically increasing graph for the first hydrolysis constant of the lanthanides.

I have given you the log k value, and the total concentration these are the two parameters that are required to plot this kind of graph because as I have shown you in this equation if you see this equation here at the bottom what we require is M total this is the unknown parameter and the pH at which we want to calculate the speciation these two things are required other thing like logk, beta values are known so if you have the information of total concentration the log k values this is the cumulative ones so if you have information of these two you can easily plot this kind of graph, and I hope you will try this kind of graphs, and you will try to plot them for different metal ions.

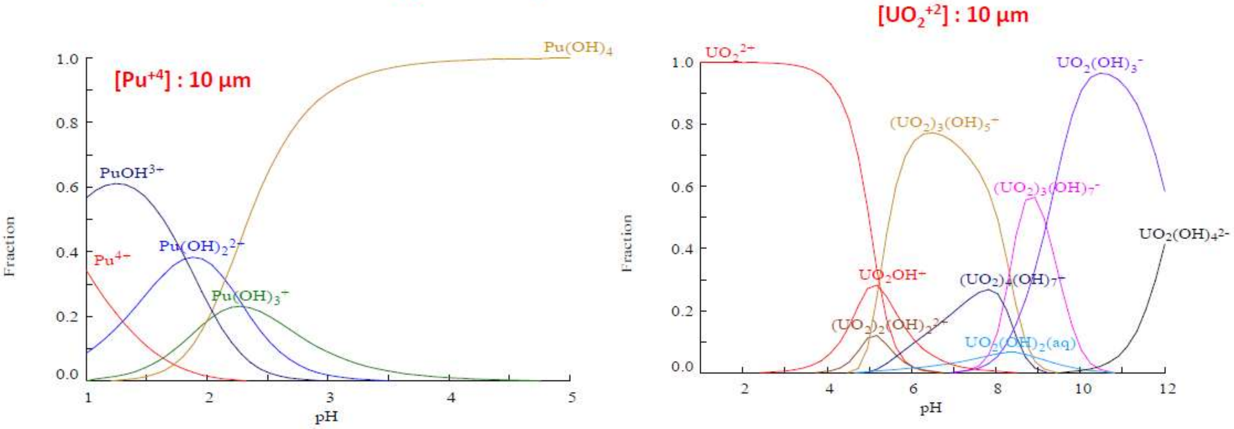
I have shown you for europium, americium, and neptunium so here I just want to discuss the case of neptunium because this is the one which I have shown you for -11.3 as I have shown you that at pH 11.3, 50% is free when I say free it is free neptunium(V), and 50% is complex, and the same situation you can see here, and this pH is nothing but around 11.3 because there is some secondary hydroxide also but very close to 11.3. so, what we can say is that before this pH this free neptunium will dominate after this pH the hydroxy species will dominate, here again, I am showing you the americium, and as you can see from the values of the first hydrolysis constant you can say that the americium is more prone to the hydrolysis compared to europium the values are less negative. so, they are more prone to hydrolysis compared to the lanthanides, here the trend again is the tetravalent is giving more hydrolysis than then actinyl (VI) ions then the trivalent, and then the lowest one we are assuming for the pentavalent.

So, again I have given you some examples of plutonium one thing I just want to mention that in all this graph I have assumed that there is no solid phase formation is happening because if your metal concentration is on the higher side, there can be precipitation or formation of solid oxide or hydroxide, then this diagram may not be truly valid so with the assumption that there is no solid phase formation all these diagrams are drawn with this assumption.

Actinide Hydrolysis

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Assuming No solid phase formation

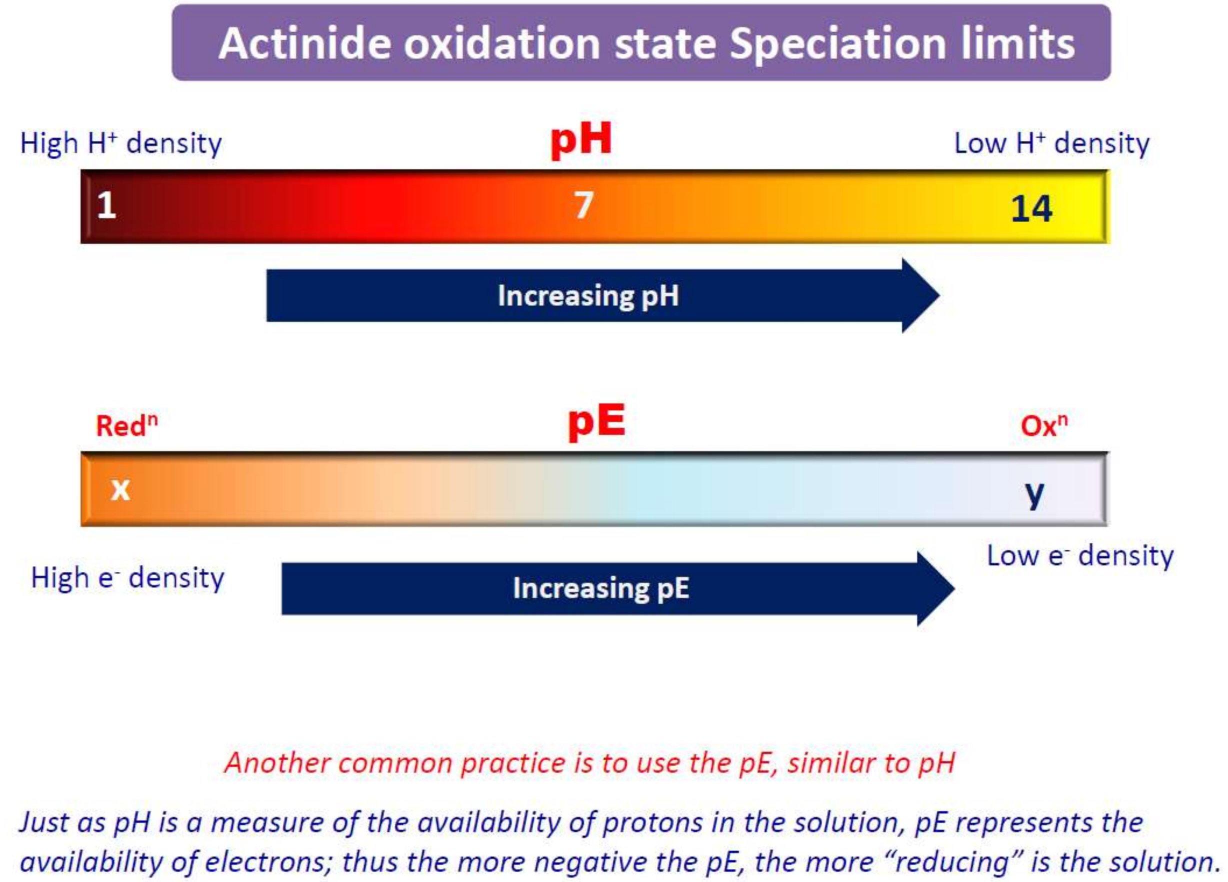


$An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+} > An^{+2}$

4+ > 3.3+ > 3+ > 2.2+ > 2+

In case of plutonium if you do not assume this assumption that there is no solid phase formation, you will get a lot of solid phases there. Again, the example of uranium was shown here, here what I want to show you is that in the case of uranium till now whatever we have shown you they are only mononuclear when I say mononuclear only one metal is involved with a certain number of hydroxy ions but when I say poly nuclear ion I can say more than one metal ions are involved so uranium is also one of this kind of species but uranium is also prone to form this kind of species you can see even at a pH circum-neutral pH less than 6, it is forming this kind of complexes in which more than one uranium moieties are coming together to form this kind of hydrolyzed complex. So, with this now we have an idea that okay we are having a metal ion we put into the solution, and if it is going to get some kind of reaction or some kind of hydrolysis at what pH it will happen, and you can easily plot or you can get some idea depending on the first hydrolysis constant that at what pH I should start my experiment, and at what pH they will just start from the hydrolyzed species.

So, I have information about the speciation diagram that what species or what hydrolyzed species, in particular, will exist at a given pH but as we have read in the previous that when we talk about these actinides they have variable oxidation states, + 7 we are not talking much because they are in highly alkaline media so this we are not talking much so we can for the time being we just assume that the oxidation state from even nobelium we are not talking much so you can say from + 3 to + 6, and when we say + 6 again it is in the form of linear dioxo cation i.e. AnO2+ for pentavalent or AnO22+ for hexavalent, now we have information of their hydrolysis, what is the trend of their hydrolysis, but since they are having different oxidation states also, how these oxidation states are varying in solution? or do we have any information about the oxidation state that can be present in water at a given condition when I say I mean that certain pE value what is pE that will try to understand the term pE, and what do I mean by the term pE?



Actinide oxidation state Speciation limits

High H^+ density

pH

Low H^+ density

1

7

14

Increasing pH

Red^n

pE

Ox^n

x

y

High e^- density

Increasing pE

Low e^- density

Another common practice is to use the pE, similar to pH

Just as pH is a measure of the availability of protons in the solution, pE represents the availability of electrons; thus the more negative the pE, the more "reducing" is the solution.

So, let us assume for simplicity that you have a pH, that we all know that what pH means is the -log of activity of a proton. So, we all know that pH 7 is neutral, and when we increase the pH to the higher side that is in the range from 7 to 14 we have low proton density or we are saying that the solution is becoming less, and less acidic, and when we are saying that, we are decreasing the pH. what do we mean? That is okay the pH is going to be decreased which means, we have high proton density, like the pH scale which we are using to get information about the hydrolyzed species. can we have some sort of scale in which we talk about the electrons? Or the availability of electrons or the electron activity so you can say very similar to pH. if there exists some scale which I can say pE which is nothing but -log you can say the activity of electrons although the electrons do not exist in the media assume that you have certain sources that somehow have some kind of redox couple, that can give some electron into the media we will talk about this in the later but assume that you have some electron, and we can make this kind of scale that is called pE.

what will happen as the pE will increase? what will happen when the number of electrons gets reduced or you can say there is less electron density. what do I mean by less electron density, that this condition is becoming an oxidizing condition, and when the pE is getting decreased, what do I mean that when your pE is on the lower side? I have not given the values of the pE what is the range we are talking about we will discuss it in the later part but, suppose you have a certain range from x to y your pE is decreased when your pE is getting decreased what will happen that the abundance of electron? electron density will increase so here the conditions are more, and more reduced so you can always compare the pH. whenever you are a bit confused so then you can always compare with the pH scale and proton availability. when we are reducing the pE we are going to the reducing condition, and when we are increasing the pE we are going to the oxidizing condition okay so if we can use this kind of variable similar to the pH we can always get information about the redox behavior so we will continue for this pH, and pe relationship, and we will see that how these variables will change the redox activity as well as the hydrolysis properties of the metal ion mainly actinide into the solution, and thank you for listening.

Thank you.

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