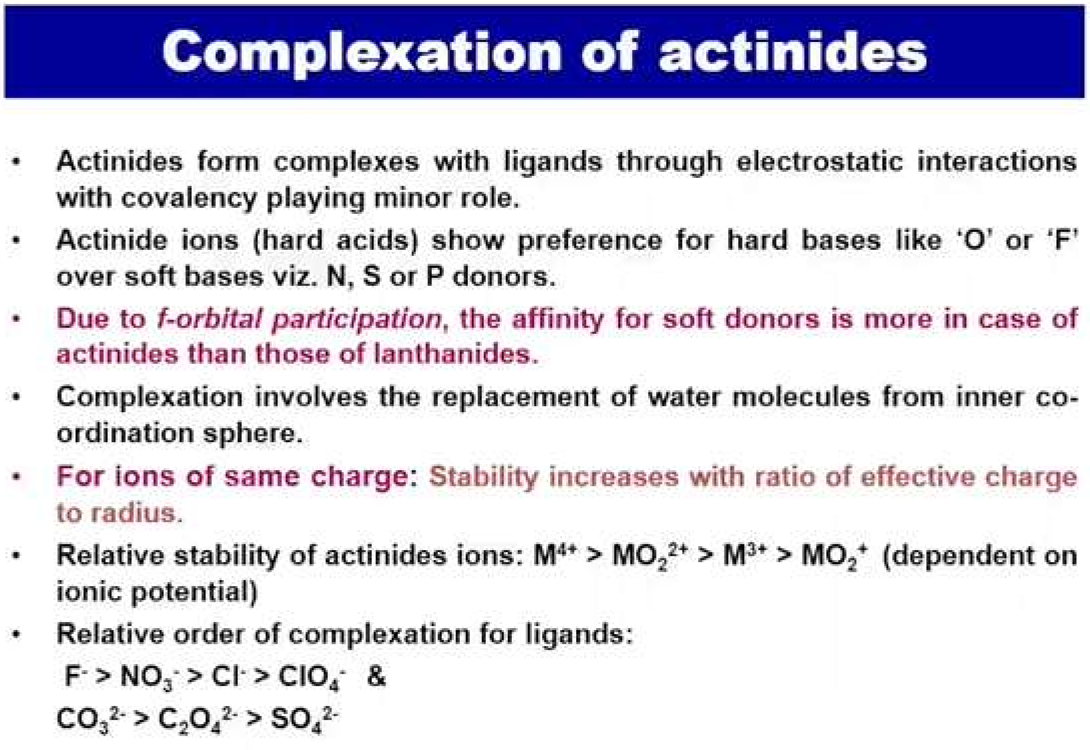
Course Name: Nuclear and Radiochemistry
Professor Name: Prof. P. K. Mohapatra
Department Name: Radiochemistry Division
Institute Name: Homi Bhabha National Institute
Week – 10
Lecture - 46

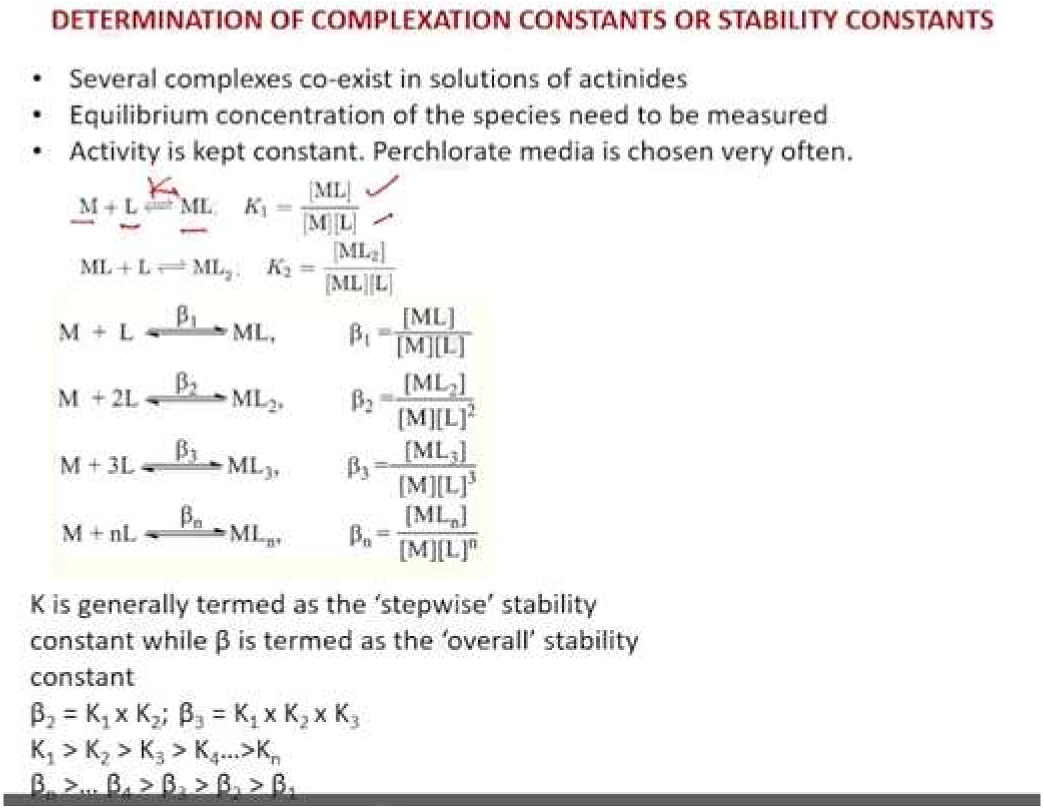
After we are familiar with the chemistry of the early actinides like uranium, neptunium, plutonium and americium, it is required now to have some discussion on the complexation of actinides which is very important in the nuclear fuel cycle applications of actinides. First, actinides form complexes with the ligands through electrostatic interactions like ion-ion as well as ion-dipole interactions. In some cases, covalency is playing also a role but to a very minor extent. This covalency becomes somewhat important in case of the early actinides and it is not that much important when we go for the heavy actinides. Now coming to the actinide-ion complexation, mostly we know these actinides are hard acids because of their high charge and they show preference for hard bases like the oxygen or fluorine type of donor atoms over the soft bases such as nitrogen, sulfur or phosphorus donor atoms. Again due to the f-orbital participation, the affinity for soft donors is more in case of the actinides than that of the lanthanides and this has been the basis of the separation of trivalent actinides from the trivalent lanthanides which we will be discussing in subsequent lecture.



Complexation of actinides

- Actinides form complexes with ligands through electrostatic interactions with covalency playing minor role.
- Actinide ions (hard acids) show preference for hard bases like ‘O’ or ‘F’ over soft bases viz. N, S or P donors.
- Due to *f-orbital participation*, the affinity for soft donors is more in case of actinides than those of lanthanides.
- Complexation involves the replacement of water molecules from inner co-ordination sphere.
- For ions of same charge: Stability increases with ratio of effective charge to radius.
- Relative stability of actinides ions: $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$ (dependent on ionic potential)
- Relative order of complexation for ligands:
  $F^- > NO_3^- > Cl^- > ClO_4^-$ &
  $CO_3^{2-} > C_2O_4^{2-} > SO_4^{2-}$

The complexation of actinides involves the replacement of water molecules from the inner coordination sphere. As we know, the actinides having very high charge that is either +3, +4 or in some cases even +5 and +6 charge. So, there is a tendency of strong hydration of these actinide-ions. As we know from the ionic species of the actinides, the +5 and +6 ions (they) are undergoing hydrolysis to give the actinyl ions. So, mainly when we are talking about the hydration of actinide-ions, we refer to the +3 and +4 oxidation states of the actinides. Then for the ions of the same charge, the stability increases with the ratio of the effective charge to reduce that is the ionic potential that is the heavier actinides will have a stronger complexation than the lighter actinides. Now when we are having different ionic species of the actinides that is the +3, +4, +5 and +6 oxidation states with ionic species of An^{3+}, An^{4+}, AnO_2^+ or AnO_2^{2+}, respectively, then the relative stability of these ions will be $M^{4+} > MO_2^{2+} > M^{3+}$ which in turn is greater than that of MO_2^+ that is the actinyl(V) ion. Relative order of the complexation for the ligands is given as below that is floride ion forms a very very strong complex compared to (the) nitrate (ion) which in turn forms a stronger complex compared to (the) chloride ion and which in turn, forms a stronger complex compared to the perchlorate ion. So, these are the singly charged anions and for the doubly charged anions like carbonate, oxalate and sulfate, the order of complexation is carbonate forms a stronger complex than the oxalate which in turn forms a stronger complex than sulfate. And these are for the inorganic ions I am discussing and for the organic ions again there will be a separate trend which I will be discussing in the subsequent part of the lecture.



DETERMINATION OF COMPLEXATION CONSTANTS OR STABILITY CONSTANTS

- Several complexes co-exist in solutions of actinides
- Equilibrium concentration of the species need to be measured
- Activity is kept constant. Perchlorate media is chosen very often.

$$\underline{M} + \underline{L} \overset{K_1}{\rightleftharpoons} \underline{ML} \qquad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$M + L \xrightleftharpoons{\beta_1} ML, \qquad \beta_1 = \frac{[ML]}{[M][L]}$$

$$M + 2L \xrightleftharpoons{\beta_2} ML_2, \qquad \beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$M + 3L \xrightleftharpoons{\beta_3} ML_3, \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3}$$

$$M + nL \xrightleftharpoons{\beta_n} ML_n, \qquad \beta_n = \frac{[ML_n]}{[M][L]^n}$$

K is generally termed as the 'stepwise' stability constant while β is termed as the 'overall' stability constant

$\beta_2 = K_1 \times K_2$; $\beta_3 = K_1 \times K_2 \times K_3$

$K_1 > K_2 > K_3 > K_4 ... > K_n$

$\beta_n > ... \beta_4 > \beta_3 > \beta_2 > \beta_1$

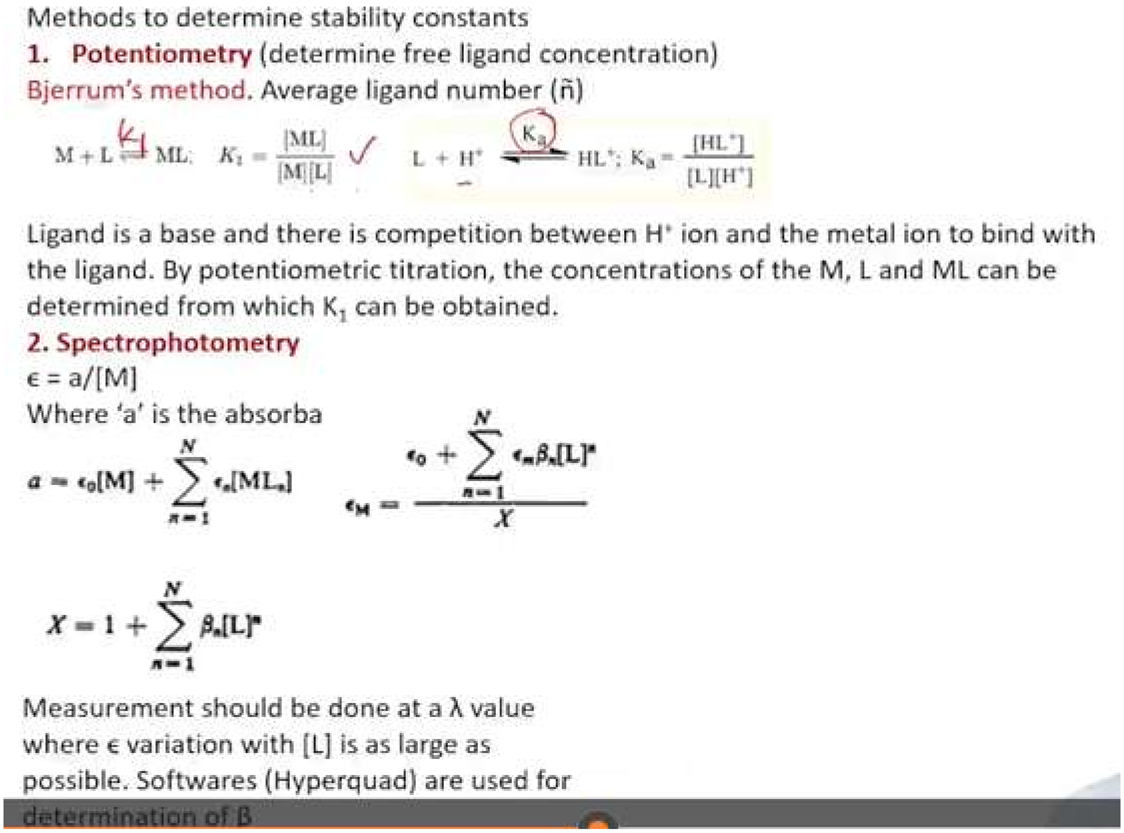
Now before we go to the complex formation of the actinides, let us discuss about the stability of the actinides and how the stability constants are determined. What we are interested in is about the basic knowledge of determination of the stability constants. Now as we know, because of the strong positive charge on the actinide ions, they can form several complexes in the aqueous medium. Suppose we take M as the actinide ion, it reacts with the ligand L to give the complex ML and this equilibrium reaction that is M plus L giving ML is given defined by a stability constant which is K_1 which is defined as K_1 equal to the concentration of ML (which is the complex) formed divided by the product of the concentrations of the metal ion as well as that of the ligand which is given in the denominator.

$$M + L \overset{K_1}{===} ML$$

Now if we are forming another complex with this particular complex that is ML is reacting with another ligand L, in that case the complex formed is ML_2 and for this the equilibrium constant is termed as K_2 which is given as ML_2 concentration divided by the product of the concentration of ML and the ligand concentration.

$$ML + L \overset{K_2}{===} ML_2$$

So, this is how these K_1 and K_2 are defined and similarly, we can have for the nth complex of the metal ion the complex formation constant as K_n. These complex formation constants are termed as the stepwise stability constants or the stepwise formation constants because here the complexation is taking place one step at a time that is first you have ML complex then you have ML_2 complex then you have the ML_3 complex and so on. Now if the complex formation is taking place where the metal ion is reacting with two ligands at the same time giving the complex ML_2 then this is called the overall complex formation constants or it is defined as β_2 in this case. You can appreciate here that the β_1 is nothing but the same as the K_1 where we have the same equilibrium but for the β_2 is different than that of the K_2 because in this case we are considering the complex formation of the metal ion reacting at one stage or at one time with the two molecules of the ligand forming the complex ML_2. So, in that case, the overall complex formation constant β_2 is given by ML_2 concentration divided by the concentration of M multiplied by the concentration of L raised to the power 2. So, this β_2 is defined like this and similar way β_3 up to β_n can be defined. Now the β_2 is nothing but the product of K_1 and K_2. As you can see here, if you multiply K_1 and K_2 you get the β_2 and similarly β_3 is the product of K_1 into K_2 into K_3 and in case of stepwise stability constants always we have the K_1 larger than that of the K_2 which in turn larger than that of the K_3 and so on and so forth. That is because of the reason that once the one complex is formed that is you form the complex ML the charge on the metal ion is partially neutralized by the ligand and what the second ligand sees is relatively lower charge than that of the first ligand has seen. And also, there is a statistical factor because for the first ligand all the coordinating sites are available. On the other hand, for the second ligand all the coordination sites minus 1 is available for complex formation. So, in view of this, the K_2 is smaller than that of K_1 and same way K_3 is smaller than that of K_2 and so on and so forth. Now on the other hand, for the overall complex formation constants the β_n which is the complex formation constant of the nth complex which is greater than that of the complex formation constant for the $(n-1)^{th}$ complex that is $ML_{(n-1)}$ defined as $\beta_{(n-1)}$ and same way if you come to the fourth overall complex formation constant β_4 is greater than β_3 which is in term greater than β_2 and this is greater than β_1. So, this is how the complex formation constants are defined.



Methods to determine stability constants

1. **Potentiometry** (determine free ligand concentration)

Bjerrum's method. Average ligand number (ñ)

M + L $\overset{K_1}{\rightleftharpoons}$ ML; $K_1 = \frac{[ML]}{[M][L]}$ ✓ L + H$^+$ $\overset{\boxed{K_a}}{\rightleftharpoons}$ HL$^+$; $K_a = \frac{[HL^+]}{[L][H^+]}$

Ligand is a base and there is competition between H$^+$ ion and the metal ion to bind with the ligand. By potentiometric titration, the concentrations of the M, L and ML can be determined from which K_1 can be obtained.

2. **Spectrophotometry**

$\epsilon = a/[M]$

Where 'a' is the absorba

$$a = \epsilon_0[M] + \sum_{n=1}^{N} \epsilon_n[ML_n] \qquad \epsilon_M = \frac{\epsilon_0 + \sum_{n=1}^{N} \epsilon_n \beta_n [L]^n}{X}$$

$$X = 1 + \sum_{n=1}^{N} \beta_n [L]^n$$

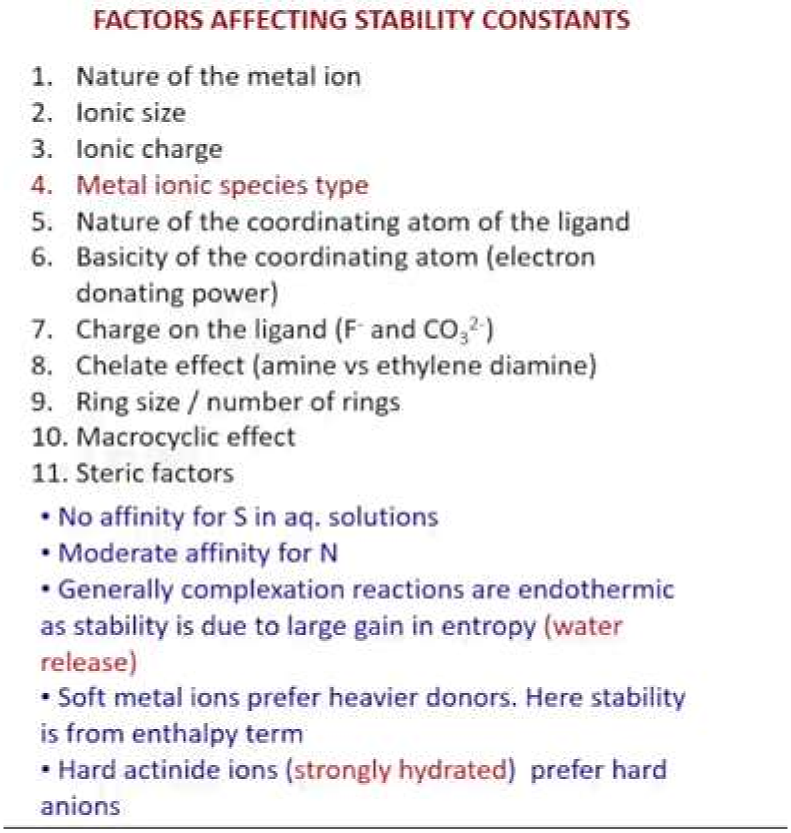
Measurement should be done at a λ value where ϵ variation with [L] is as large as possible. Softwares (Hyperquad) are used for determination of β

Now what are the methods to determine the stability constants or the complex formation constants? There are general methods for this. Now one is called the potentiometric method which is also known as the Bjerrum's method where you find out the average ligand number and as already mentioned here for the first stepwise formation constant that is the K_1 value we have this equilibrium reaction given here and also there is a competing reaction with the ligand where the ligand also interacts with the proton which is there in the aqueous phase and this is called the proton association constants defined as the K_a value of the ligand and the K_a is given as the concentration of HL^+ divided by the product of the ligand concentration and hydrogen ion concentration.

$$K_a = \frac{[HL^+]}{[L][H^+]}$$

As you know that (the) ligand is a base so there is always a competition between the hydrogen ion and the metal ion to bind with the ligand. Now by potentiometric titration the concentration of the metal ion, the ligand and the ML species can be determined from which the complex formation constant (in this case the K_1) can be obtained. Similar way the complexation constants for the other complexes that is ML_2, ML_3 up to ML_n also can be obtained but for that we also need some software which will be doing the computation of the complex formation constants. Another method which is used for the complex formation (very generally used) is the spectrophotometry where we take the metal ion and mix with the ligand.

Here, in this case, this metal ligand complex should be forming a colored complex and that is how when we measure the absorbance versus the lambda value we get some absorption spectra like this and by varying the ligand concentration keeping the metal ion concentration constant or the vice versa we can find out different absorbance values and from which we can find out the complex formation constants.



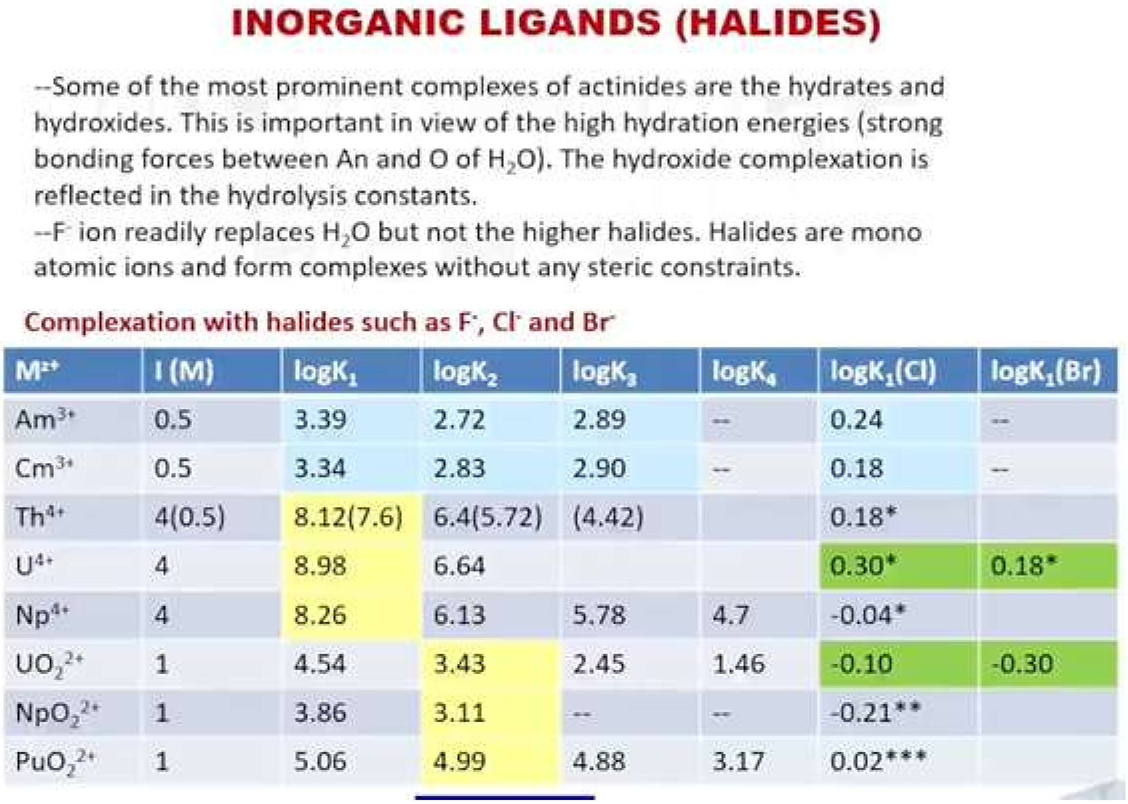
FACTORS AFFECTING STABILITY CONSTANTS

1. Nature of the metal ion
2. Ionic size
3. Ionic charge
4. Metal ionic species type
5. Nature of the coordinating atom of the ligand
6. Basicity of the coordinating atom (electron donating power)
7. Charge on the ligand (F^- and CO_3^{2-})
8. Chelate effect (amine vs ethylene diamine)
9. Ring size / number of rings
10. Macrocyclic effect
11. Steric factors

- No affinity for S in aq. solutions
- Moderate affinity for N
- Generally complexation reactions are endothermic as stability is due to large gain in entropy (water release)
- Soft metal ions prefer heavier donors. Here stability is from enthalpy term
- Hard actinide ions (strongly hydrated) prefer hard anions

Now which are the factors that affect the stability constants? The nature of the metal ion that is whether the metal ion is a soft metal ion or a hard metal ion so that matters a lot. Ionic size, as I mentioned, for similar charge of the metal ion the ionic size can be different because of the actinide contraction in our case particularly. Ionic charge the actinides can have different charge like +2, +3, +4, +5 and +6. Then ionic species type what type of ionic species whether you have MO_2^+, MO_2^{2+}, or the corresponding cations like M^{5+} or M^{6+} so that also matters a lot and that decides also on the stability of the complexes. Nature of the coordinating atom of the ligand that is whether you have an oxygen atom or a nitrogen atom or a sulfur atom or a halogen atom like fluoride, chloride, etc., this also decides the complex formation. Basicity of the coordinating atom that is the electron donating power in a ligand. Then charge on the ligand that is whether we have a single charge like in fluoride (F^-) or a double charged ligand like carbonate (CO_3^{2-}) that also matters a lot. So, naturally carbonate forms a stronger complex because of 2 minus charge as compared to the fluoride which has a single minus charge and also the chelate effect that is whether the ligand is monodentate or bidentate.

For example, we have this ligand like amine coordinating site is the nitrogen and also, we have ethylene diamine. This is ethylene diamine and this case also the coordinating site is the nitrogen atoms but this (ethylene diamine) can form a chelate complex. So, if I have a metal here, so this can bind like this and this is a chelate complex and similarly if I have amine complex of the metal, so this is how these two nitrogens are coordinated with two amines and for the ethylene diamine also I have two nitrogen atoms coordinating but the chelate formation in case of the ethylene diamine gives a stronger complex as compared to the two amine complexes shown here. Next is the ring size and the number of rings. Here we have got a five-membered ring for ethylene diamine. Some cases we may have a four-membered ring, some cases we may have a six-membered ring. So, the stability of the complex again depends on the ring size of the chelates. Then there is something called a macrocyclic effect. So we have this crown ether type ligands. For example, I take this 12-crown-4. This forms a complex with a metal ion, say lithium plus. So, in this case it is stabilized because of the macrocyclic effect and lithium forms a very strong complex with a 12-crown-4. There are also steric factors if the ligand is having some functional groups which are binding and also some side chains which are affecting the stereochemistry or the approach of the binding donor atom. In that case, there are steric factors which are affecting the complex formation constants. So that is how the complex formation constants can be lower in such cases where the steric factors are hindering the complexation. Now the affinity of the sulfur in the aqueous solution is almost not there or we can say there is no affinity for sulfur. That is why we do not study many of these sulfur donor ligands in the aqueous solution. There is moderate affinity for the nitrogen donor ligands and generally the complexation reactions are endothermic as the stability is due to the large gain in the entropy that is the water release as we have already mentioned before these actinides are having relatively high charge and they are strongly hydrated. So, when the complex is formed in that case the ligands are to replace the water molecules in the inner coordination sphere and that is leading to very strong entropy gain because the water molecules are released. Then soft metal ions prefer heavier donors and here the stability is from the enthalpy term. Heavier donor means compared to oxygen and sulfur. Naturally, sulfur will have a preference for the soft metal ion compared to oxygen. Hard actinide ions which are strongly hydrated prefer hard anions like fluoride.



INORGANIC LIGANDS (HALIDES)

--Some of the most prominent complexes of actinides are the hydrates and hydroxides. This is important in view of the high hydration energies (strong bonding forces between An and O of H_2O). The hydroxide complexation is reflected in the hydrolysis constants.

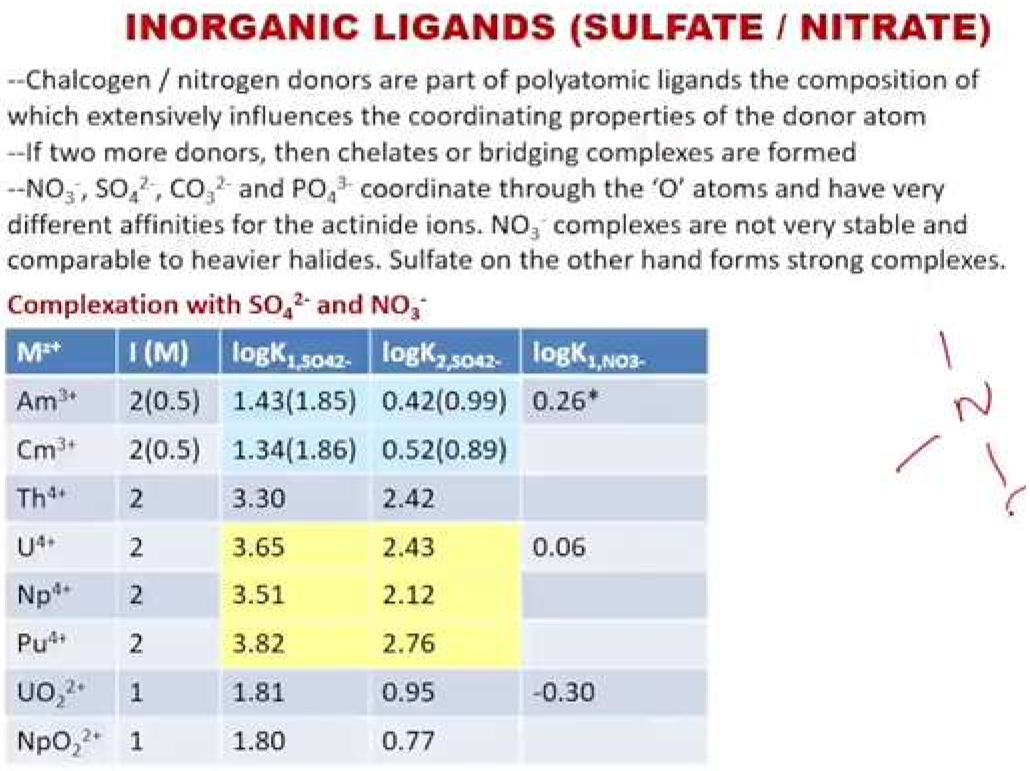
--F^- ion readily replaces H_2O but not the higher halides. Halides are mono atomic ions and form complexes without any steric constraints.

Complexation with halides such as F^-, Cl^- and Br^-

M^{z+}	I (M)	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_1$(Cl)	$\log K_1$(Br)
Am^{3+}	0.5	3.39	2.72	2.89	--	0.24	--
Cm^{3+}	0.5	3.34	2.83	2.90	--	0.18	--
Th^{4+}	4(0.5)	8.12(7.6)	6.4(5.72)	(4.42)		0.18*	
U^{4+}	4	8.98	6.64			0.30*	0.18*
Np^{4+}	4	8.26	6.13	5.78	4.7	-0.04*	
UO_2^{2+}	1	4.54	3.43	2.45	1.46	-0.10	-0.30
NpO_2^{2+}	1	3.86	3.11	--	--	-0.21**	
PuO_2^{2+}	1	5.06	4.99	4.88	3.17	0.02***	

Now coming to the inorganic ligands like halides. Some of the most prominent complexes of actinides are the hydrates or hydroxides. This is very important in view of the very high hydration energies of the actinide ions which are in the plus 3 or plus 4 oxidation states and the hydroxide complexation is reflected in the hydrolysis constants. This will be discussed in a separate chapter so I will not go deep into this. Now coming to the halides. The fluoride ion readily replaces the water but not the higher halides like the chlorides or bromides. So the halides are monoatomic anions and form complexes without any steric constraint.

Now here this table which is given below, it gives a complexation of halides such as fluoride, chloride and bromides. The first column gives the metal ions, the second column the ionic strength, the third, fourth and fifth and sixth column gives the log K_1, K_2, K_3 and K_4 values for (the) fluoride (ion). The last but one column is for the chloride ion complex formation and the last column is about the bromide complex formation. Now we will just see how this complex formation constants with fluoride, chloride and bromide is there for the actinide ions. First let us take the trivalent actinide ions that is americium 3 plus and curium 3 plus. For simplicity we have taken data for a particular ionic strength which is constant that is 0.5 M ionic strength and you see the log K values. There is no clear trend here though we expect that the Cm^{3+} should have higher stability constant as compared to Am^{3+}. Though it is not the case. On the other hand, the log K_2 value for Cm^{3+} is higher than that of the Am^{3+}. Same also is the trend for the log K_3. So, overall, we can say that the complex formation constants of americium and curium in the trivalent oxidation state are nearly comparable. Now you come to the tetravalent oxidation state that is Th^{4+}, U^{4+} and Np^{4+}. For comparison purpose, we have taken the ionic strength constant for them as 4 M and you can see here that the thorium value is 8.12 for the log K_1 which increases significantly for uranium that is 8.98 but for Np^{4+} it decreases. So, the increase of the log K_1 value from Th^{4+} to U^{4+} is understandable because of the higher ionic potential but for the Np^{4+} there is a strong decrease and this is not explainable. This all because of strange complexation behavior of the neptunium ion. Expectedly neptunium should have higher complex formation constant than that of U^{4+} but we will see in the subsequent lectures that Np^{4+} behaves somewhat different manner compared to the other actinide ions. And the same also for the Np(VI), when you have NpO_2^{2+}. Come here for the next 3 ions with a +6 oxidation states at 1 M ionic strength we find that the uranyl ion complex formation constant of the log K_1 value is 4.54 which should have increased for neptunyl ion (neptunium(VI)) but the value has decreased to 3.86 which, on the other hand, has increased significantly for the plutonyl ion that is PuO_2^{2+} to 5.06. Same is the trend for the log K_2 values and also for the log K_3 values for which the Np(VI) data is not there but you can see that the uranium complex formation constant is significantly lower than that of the plutonyl ion complex formation constant which is explainable from the ionic potential. Now coming to the chloride ion complexation compared to the fluoride ion you find that the complex formation constants are significantly lower. Find that for the trivalent as well as the tetravalent ions and also the hexavalent ions you find that the complex formation constants are significantly lower compared to what is seen for the fluoride ion and with bromide ion again you find even lower complex formation constants. Only the log K_1 values are given for the fluoride and bromide ion.



INORGANIC LIGANDS (SULFATE / NITRATE)

--Chalcogen / nitrogen donors are part of polyatomic ligands the composition of which extensively influences the coordinating properties of the donor atom

--If two more donors, then chelates or bridging complexes are formed

--NO_3^-, SO_4^{2-}, CO_3^{2-} and PO_4^{3-} coordinate through the 'O' atoms and have very different affinities for the actinide ions. NO_3^- complexes are not very stable and comparable to heavier halides. Sulfate on the other hand forms strong complexes.

Complexation with SO_4^{2-} and NO_3^-

M^{z+}	I (M)	$\log K_{1,SO42-}$	$\log K_{2,SO42-}$	$\log K_{1,NO3-}$
Am^{3+}	2(0.5)	1.43(1.85)	0.42(0.99)	0.26*
Cm^{3+}	2(0.5)	1.34(1.86)	0.52(0.89)	
Th^{4+}	2	3.30	2.42	
U^{4+}	2	3.65	2.43	0.06
Np^{4+}	2	3.51	2.12	
Pu^{4+}	2	3.82	2.76	
UO_2^{2+}	1	1.81	0.95	-0.30
NpO_2^{2+}	1	1.80	0.77	

Now we come to the other inorganic ligands like sulfate and nitrate. So, the sulfate ions (they) form much stronger complexes as compared to the nitrate that is obvious because sulfate is having 2 minus charge as compared to the nitrate ion which is having a single charge and also there are the number of donor atoms which are participating in case of the sulfate many times it is 2 compared to the nitrate. There are of course examples where the nitrate ion also acts as a bidentate ligand like you have this 3 oxygens attached to the nitrogen in case of the nitrate and sometimes this O^- is coordinating to the metal ion (and in) some cases you have even the metal ion is binding to 2 oxygens of the nitrate. So, this type of scenario also is there so you have both monodentate as well as bidentate complexation in case of the nitrate but the sulfate because of the 2 minus charge it forms many cases bidentate complexes. Now in case of nitrate / sulfate the coordination is through the oxygen atoms and they have very high affinity for the actinide ions but compared to the nitrate ion (the) sulfate has a greater affinity and here the log K_1 and log K_2 values for the sulfate ion is given for the actinide ions and the last column is about the nitrate ion. You can see that this nitrate ion complex formation constants are definitely much lower than that of the sulfate ion. For Am^{3+} and Cm^{3+} ions you find again Cm^{3+} is having lower complex formation constant for the log K_1 value when the ionic strength is 2 M but for 0.5 M ionic strength, the complex formation constants are more or less same that is 1.85 and 1.86 and the log K_2 values for Cm^{3+} is larger compared to that of Am^{3+}. On the other hand, log K_2 value for the Cm^{3+} is lower as compared to that of Am^{3+} for the sulfate ion. This is really intriguing (that) the complex formation constants of americium and curium are more or less comparable, we can say, in many cases. Now coming to the tetravalent actinide ions Th^{4+}, U^{4+}, Np^{4+} and Pu^{4+}: all cases the ionic strength has been kept as 2 M and we see here in this case from Th^{4+} to U^{4+} the log K_1 values are increasing from 3.30 to 6.65 which decreases in case of the Np^{4+} as we have seen in case of the fluoride (ion) and the same observation was also seen for the Pu^{4+} that the log K_1 values increases as compared to that of U^{4+} as well as Np^{4+}. So the Pu^{4+} complex formation constant is higher can be explained on the basis of its very high ionic potential but the Np^{4+} log K_1 value is in between that of U^{4+} and Pu^{4+} and this is some sort of an anomaly. Same is the trend we can see for the log K_2 values where the Np^{4+} complex formation constant is in between that of U^{4+} and Pu^{4+}. Now coming to the hexavalent ions, the uranyl ion's first complex formation constant with the sulfate ion is comparable to that of the neptunyl ion. On the other hand, the second complex formation constant that is the log K_2 value is significantly lower as compared to that has been reported for the uranyl ion. The complex formation constants with the uranyl ion with the nitrate is very very low compared to what we have seen for the sulfate ion and also it is lower than that of the halides like fluoride but it is comparable to that of the bromide ion, the log K_1 values. Thank you.

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