Course Name: Nuclear and Radiochemistry
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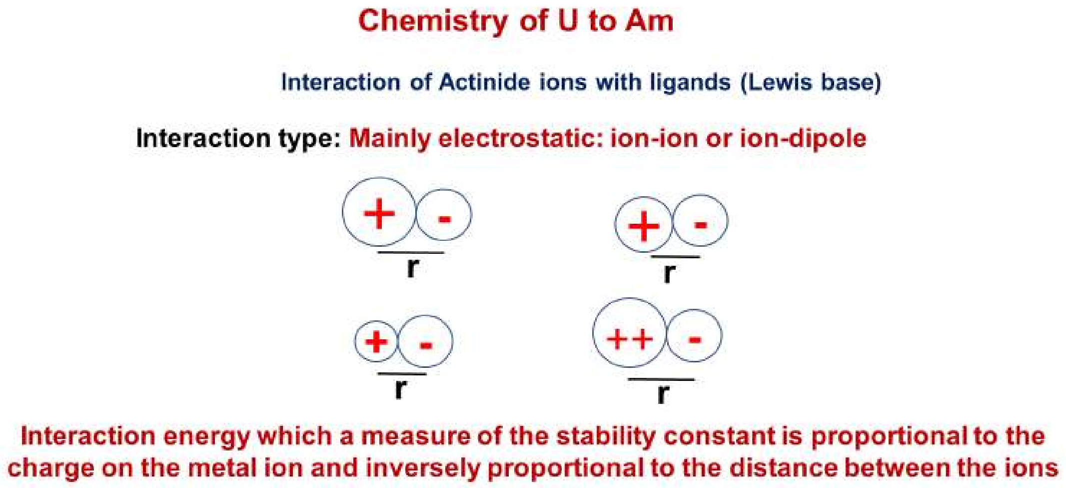
Week – 09
Lecture - 44

We have previously discussed about the actinides, their production, the discovery of some of the actinides and also their electronic configuration. Now, as I have already mentioned before, the actinides have relevance in the nuclear fuel cycle. So we need to understand the chemistry of actinides, particularly those which are relevant for the nuclear fuel cycle. So in this lecture, I will be discussing about the chemistry of uranium to americium. That means uranium, neptunium, plutonium and americium. These four elements mainly, they are of great relevance in the nuclear fuel cycle. Other details will be covered in separate lectures. This lecture is just on the broad chemistry of uranium to americium. Now when we are talking about the chemistry of actinides, we also should know about their complexation, that is the interaction of actinide ions with the ligands, which are mostly Lewis bases. The interaction with actinides are mainly electrostatic, that is ion-ion or ion-dipole.



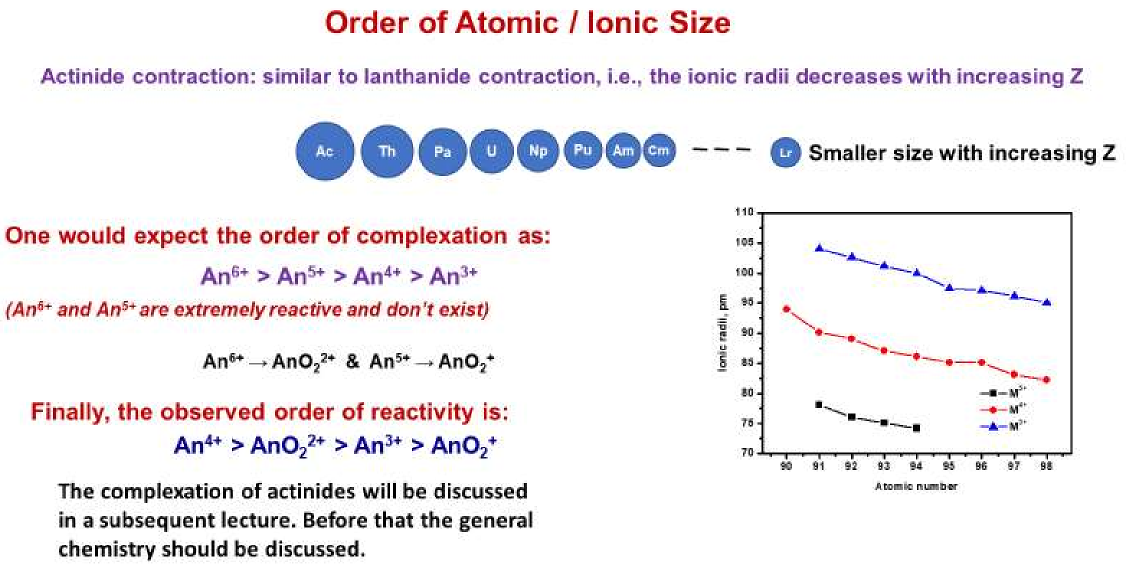
Chemistry of U to Am

Interaction of Actinide ions with ligands (Lewis base)

Interaction type: Mainly electrostatic: ion-ion or ion-dipole

Interaction energy which a measure of the stability constant is proportional to the charge on the metal ion and inversely proportional to the distance between the ions

So all the actinide metal ions are ions and we have the ligands which can be neutral ligand, in such case we have the ion-dipole interaction and if it is anionic ligand, then it is the ion-ion interaction. Now this interaction energy is a measure of the stability constant and it is proportional to the charge on the metal ion and also inversely proportional to the distance between the ions. I have shown some schematic here in which the different actinide ions are represented by either plus or plus plus (2+), that means multiple charged metal ions and the ligand for simplicity I have taken just minus for all cases. I have taken four cases where I have tried to show the size of the metal ion as different. The first case, the size of the metal ion is bigger than that of the second one, where the size is smaller and in case of the third one, the ligand size is bigger than that of the metal ion and in the fourth case, we have the doubly charged metal ion, which has a bigger size than that of the donor group of the ligand.



Order of Atomic / Ionic Size

Actinide contraction: similar to lanthanide contraction, i.e., the ionic radii decreases with increasing Z

Ac Th Pa U Np Pu Am Cm --- Lr Smaller size with increasing Z

One would expect the order of complexation as:

$An^{6+} > An^{5+} > An^{4+} > An^{3+}$

(An^{6+} and An^{5+} are extremely reactive and don't exist)

$An^{6+} \rightarrow AnO_2^{2+}$ & $An^{5+} \rightarrow AnO_2^{+}$

Finally, the observed order of reactivity is:

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

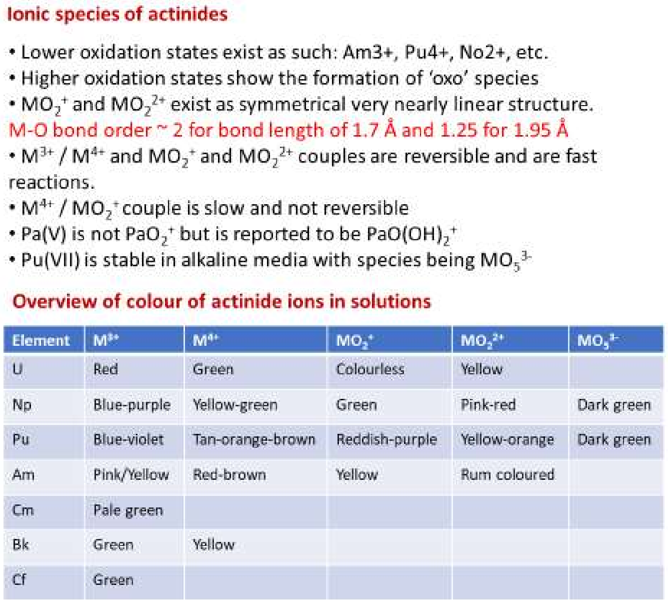
The complexation of actinides will be discussed in a subsequent lecture. Before that the general chemistry should be discussed.

As you can see, the radius between the metal ion and the ligating ion is varying depending on the size of the metal ion. So now as I have mentioned, the stability of the metal complexes will depend not only on the charge but also the distance between the ions. Now actinides, as we know that they are from actinium to lawrencium. The size of the actinides, when we take a particular ionic species, say plus three oxidation state, then the size of the actinides will be changing. This phenomenon is called the actinide contraction, that is the ionic radii decreases with increasing charge of the actinide ions. This is similar to the lanthanide contraction and it has a great significance in the complexation. That means the heavier actinide will form a stronger complex compared to the lighter actinide. So this is what will be discussed in subsequent part of this lecture. The ionic species of the actinides I will be discussing. There are different type of species.

Now considering that the actinides have different oxidation states, say from plus three to plus six, they are the very commonly available oxidation state of the actinides. And you can see that if it is a plus six oxidation state, it will form a definitely stronger complex than the plus five oxidation state, which will form a stronger complex with the plus four oxidation state, which will form a stronger complex system than the plus three oxidation state. However, the actinides plus six (6+) oxidation state and actinide in the plus five (5+) oxidation state, they're extremely reactive in water and they don't exist at the plus six oxidation state, the actinide plus six, but they exist as the actinyl ion that is AnO_2^{2+} ion. Similarly, An^{5+} ion in water medium is hydrolyzed and it is forming the species like AnO_2^{+} ion. So, these are the ionic species for the plus six oxidation state that is AnO_2^{2+} and the plus five oxidation state that is AnO_2^{+}.

As will be discussed in subsequent lectures, the charge on the actinide ion in the plus six oxidation state this actinyl ion is little more than three plus and that of the plus five oxidation state actinyl ion, that is AnO_2^+ is little higher than plus two. That means the observed reactivity while forming the complexes or the actinyl ion in the plus six oxidation state will be a little lower than that of the plus four actinide ion and it will be somewhat higher than that of the plus three oxidation state. Similarly, the actinyl ion in the plus five oxidation state that is AnO_2^+ ion will have somewhat higher reactivity compared to the plus two oxidation state and somewhat lower reactivity than the plus three oxidation state. So the complexation of the actinide will be discussed in a subsequent lecture. So, before that we'll be discussing the general chemistry of the actinides.

The right hand figure gives a comparison of the plus three, plus four, as well as plus five oxidation states of the actinides and it shows the ionic radii in picometer, vis-a-vis the atomic number of the actinides and as can be seen, this ionic radii is continuously decreasing for the plus three oxidation state and plus four oxidation state also. For plus five oxidation state, we see again some relatively less steep decrease, but nevertheless there is decrease in the ionic size, i.e., ionic radius. Now coming to the different ionic species of the actinides, as I mentioned in the previous slide, the lower oxidation states such as plus three, plus four and plus two, there is relatively less hydrolysis in the water medium and the actinide ions exist in those charged states.



Ionic species of actinides

- Lower oxidation states exist as such: Am3+, Pu4+, No2+, etc.
- Higher oxidation states show the formation of 'oxo' species
- MO_2^+ and MO_2^{2+} exist as symmetrical very nearly linear structure.

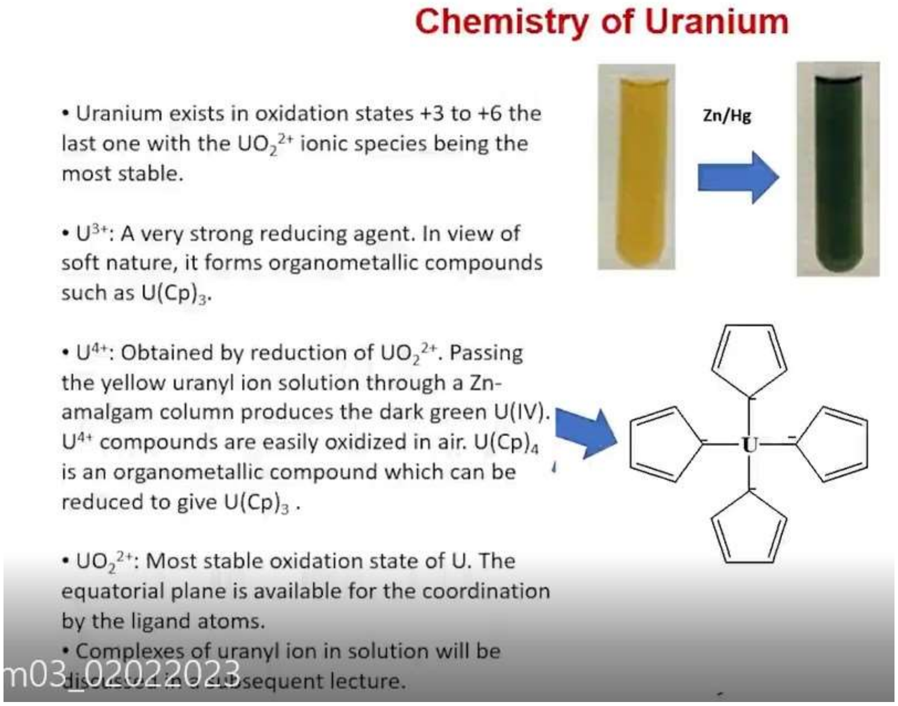
M-O bond order ~ 2 for bond length of 1.7 Å and 1.25 for 1.95 Å

- M^{3+} / M^{4+} and MO_2^+ and MO_2^{2+} couples are reversible and are fast reactions.
- M^{4+} / MO_2^+ couple is slow and not reversible
- Pa(V) is not PaO_2^+ but is reported to be $PaO(OH)_2^+$
- Pu(VII) is stable in alkaline media with species being MO_5^{3-}

Overview of colour of actinide ions in solutions

Element	M^{3+}	M^{4+}	MO_2^+	MO_2^{2+}	MO_5^{3-}
U	Red	Green	Colourless	Yellow	
Np	Blue-purple	Yellow-green	Green	Pink-red	Dark green
Pu	Blue-violet	Tan-orange-brown	Reddish-purple	Yellow-orange	Dark green
Am	Pink/Yellow	Red-brown	Yellow	Rum coloured	
Cm	Pale green				
Bk	Green	Yellow			
Cf	Green				

You can see, for example, Am^{3+}, Pu^{4+} and No^{2+}. So these are existing, these plus three, plus four and plus two oxidation charge species in the aqueous medium. On the other hand, the higher oxidation states form the oxo species as shown below, the MO_2^+ and MO_2^{2+} exist as symmetrical, nearly linear structure where the MO bond order is around two for the bond length of around 1.7 between the metal ion and the oxygen and then due to complexation, MO bond order is lower, that is if it is around 1.25 for the bond length is also elongated and we have 1.95 angstrom at the MO bond length. The ionic species like M^{3+} gets oxidized to M^{4+}. Similarly, MO_2^+ gets oxidized to MO_2^{2+} and these couples are reversible and are fast reactions are possible. On the other hand, the M^{4+} to MO_2^+ conversion, that is the tetravalent actinide to the pentavalent actinide couple is slow and it is not reversible. This is because of the bond formation between the metal and the oxygen and this is a slow process and that is why this is not reversible couple. For protactinium 5, though one can predict species like PaO2+, similar to that of neptunium pentavalent or plutonium pentavalent species, but the reported species is $PaO(OH)^{2+}$. So, this is the actual species which is existing and then reported in the aqueous medium. The Pu in the 7+ oxidation state is not stable in the normal acidic aqueous medium and is stable only in the alkaline medium, the species being MO_5^{3-}. All these actinide ions, they have different colors if taken in appreciable concentrations and I have given a table here where you can see the color of the actinides. For example, uranium in the plus three state, it is red color. Uranium in the plus four states is the green color. Uranium in plus five state is colorless and Uranium in plus six state is the well-known yellow color which we see most of the uranium compounds in yellow color. Neptunium in plus three state is a blue purple and plus four state is yellow green plus five state, that is MO_2^+, that is NpO_2^+, this is a green color. NpO_2^{2+}, this species neptunium six, oxidation state, it is pink red and the anionic species of neptunium seven, that is NpO_5^{3-} in alkaline medium is dark green color. Same also for plutonium in the plus seven oxidation state, that also we get anionic species PuO_5^{3-} and also we get a dark green color similar to the neptunium(VII) oxidation state. Bu,t generally, we don't deal with the alkaline medium, the nuclear fuel cycle, that is why it is only academic interest for the neptunium and plutonium plus seven states. On the other hand, the other oxidation states are of great relevance, for example, for plutonium mostly, plutonium three plus, that is color of blue to violet color, plutonium four plus, which has a tan orange to brown color, plutonium five, that is PuO_2^+, it has a reddish purple color and plutonium six, that is PuO_2^{2+}, it has a yellow orange color. So these are the anionic species of plutonium and americium as mostly, Am^{3+} as the anionic species, that is having a color of pink or yellow color, depending on the medium. Am4+ can also be obtained, it has a red brown color, Am(V) or AmO_2^+ plus can be done by electrochemical oxidation of americium, it has a yellow color, and Am(VI), that is AmO_2^{2+}, has a rum color in the aqueous solution. Curium exists in plus three oxidation state and it has a pale green color. Bk^{3+} in the green color, Bk is also existing in plus four oxidation state and it has yellow color. Californian has a green color. I'm covering only up to this because other actinides are produced at a very low concentration, so we'll not be dealing with this.

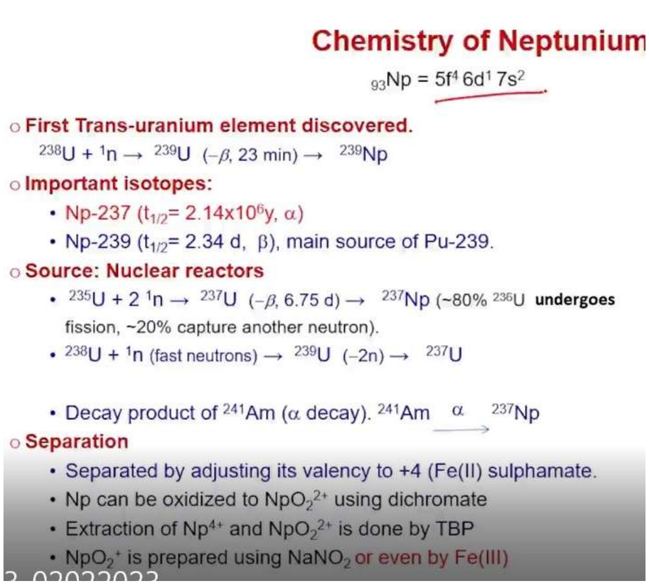


Chemistry of Uranium

- Uranium exists in oxidation states +3 to +6 the last one with the UO_2^{2+} ionic species being the most stable.
- U^{3+}: A very strong reducing agent. In view of soft nature, it forms organometallic compounds such as $U(Cp)_3$.
- U^{4+}: Obtained by reduction of UO_2^{2+}. Passing the yellow uranyl ion solution through a Zn-amalgam column produces the dark green U(IV). U^{4+} compounds are easily oxidized in air. $U(Cp)_4$ is an organometallic compound which can be reduced to give $U(Cp)_3$.
- UO_2^{2+}: Most stable oxidation state of U. The equatorial plane is available for the coordination by the ligand atoms.
- Complexes of uranyl ion in solution will be discussed in a subsequent lecture.

I summarize the chemistry of these early actinides, the chemistry of uranium. As mentioned in the previous slide, uranium exists in oxidation state +3 to +6, but the +6 oxidation state is most common, that is, UO_2^{2+} ionic species being the most stable and we are dealing with, in our chemistry labs, uranium in the +6 oxidation state. U^{3+} is a very strong reducing agent because it is not at all stable and in view of its soft nature, it can form organometallic compounds like with ligands like cyclopentadienyl and this $U(Cp)_3$ type of complexes are reported for uranium. U^{4+} is obtained by reducing uranium six oxidation state, that is, uranyl ion, by passing this yellow uranyl ion solution through a zinc amalgam column and it produces the dark green uranium four as it is shown in this figure. Now this uranium four also forms the cyclopentadienyl complex and the structure is given here where you have the four cyclopentadienyl ligands coordinating to the uranium plus four species and this can be reduced to give this $U(Cp)_3$, that is, the cyclopentadienyl complex of the uranium plus three oxidation state. These organometallic compounds are very, very unstable in air and you have to take special precautions to preserve them. As I mentioned, uranium plus six oxidation state, that is, UO_2^{2+} is the most stable oxidation state of uranium and in this case, you are having actually uranium with two axial oxygens and there is equatorial plane which is available for the coordination by the linear atoms. So, complexation of uranium ion in solution will be discussed in a subsequent lecture.

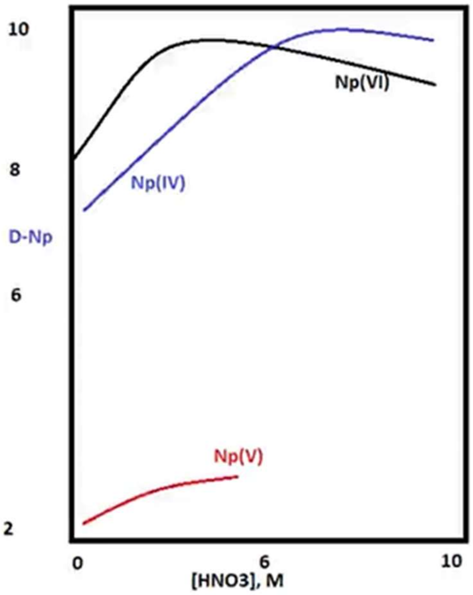
I have shown here the spectra of the uranyl ion. See, generally you get this type of pattern where you have the different bands are there and at appreciable concentration of uranium, this can be used for the estimation of uranium, but if the low concentration uranium is there, then we have to go for different methods by spectrophotometry, but we can do is we can use a coloring agent and then we can measure the optical density to find out the concentration of uranium ion. Uranyl ion gets hydrolyzed in aqueous medium. When the pH is around four to six, that region also gets hydrolyzed and at high pH values, it forms dimeric or polymeric species. I have shown this speciation diagram of uranium, you can see here up to pH four, it is uranyl ion is stable and at increasing pH values, you have the other species, the $UO_2(OH)^+$, $UO_2(OH)_2$, which is a neutral species and subsequently you have this dimeric and polymeric species at higher pH values.



Chemistry of Neptunium

$_{93}Np = 5f^4\,6d^1\,7s^2$

- **First Trans-uranium element discovered.**
  $^{238}U + {}^1n \rightarrow {}^{239}U\ (-\beta, 23\ min) \rightarrow {}^{239}Np$
- **Important isotopes:**
  - Np-237 ($t_{1/2}$= 2.14x10^6y, α)
  - Np-239 ($t_{1/2}$= 2.34 d, β), main source of Pu-239.
- **Source: Nuclear reactors**
  - $^{235}U + 2\,{}^1n \rightarrow {}^{237}U\ (-\beta, 6.75\ d) \rightarrow {}^{237}Np$ (~80% ^{236}U **undergoes** fission, ~20% capture another neutron).
  - $^{238}U + {}^1n$ (fast neutrons) $\rightarrow {}^{239}U\ (-2n) \rightarrow {}^{237}U$
  - Decay product of ^{241}Am (α decay). $^{241}Am \xrightarrow{\alpha} {}^{237}Np$
- **Separation**
  - Separated by adjusting its valency to +4 (Fe(II) sulphamate.
  - Np can be oxidized to NpO_2^{2+} using dichromate
  - Extraction of Np^{4+} and NpO_2^{2+} is done by TBP
  - NpO_2^+ is prepared using $NaNO_2$ or even by Fe(III)

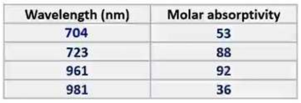


Now, coming to the chemistry of neptunium, Np has the electronic configuration as I mentioned as $5f^4$, $6d^1$ and $7s^2$. So, as per this, if all valence electrons are removed, then you can have neptunium 7 plus 7 species, which is anionic species I have just discussed in the previous slide and such species are present in alkaline medium. On the other hand, you can also have neptunium in the plus four, plus three states, that will be less stable and plus five and plus six oxidation states. As I have already mentioned, neptunium is the first trans-uranium element discovered by the reaction of ^{238}U, the neutron capture giving ^{239}U, which undergoes beta decay to produce ^{239}Np. This is how we get this ^{239}Np in the reactor and this is used in the laboratory studies, a very good quality tracer is obtained. Other important isotopes are neptunium-237. ^{237}Np particularly is very important because it has a very long half-life. Now, in the radioactive waste management, this neptunium-237 has to be necessarily separated, otherwise the waste has to be kept under the geological repository and the surveillance period will be very, very long. That I will be discussing in a separate lecture.

This ^{239}Np, as I mentioned, has the applications. That it decays to give plutonium-239, which has a lot of relevance because it's a fissile isotope of plutonium. Now, in the nuclear reactor, you can get ^{237}Np by these two reactions mentioned here. From ^{235}U you can get as well as from ^{238}U. We can get by the capture of fast neutrons for the ^{238}U and also by capture of thermal neutron, you can get it from ^{235}U. We get the ^{237}U from the ^{235}U, which undergoes beta decay to give ^{237}Np. Similarly, for the ^{238}U, capture of fast neutron gives ^{239}U and it emits two neutrons to become ^{237}U, which undergoes beta decay to give the ^{237}Np. Also, the decay product of ^{241}Am by alpha decay can give ^{237}Np. So, these are the sources of ^{237}Np and the separation of this neptunium, as I mentioned, it is required for the radioactive waste management purposes. And while doing this, this valency state of neptunium has to be adjusted so that this separation can be done by solvent extraction or ion exchange methods. Neptunium can be converted to the plus four valency by ferrous sulphamate. Neptunium can be oxidized to the plus six oxidation state by dichromate and this neptunium plus four and plus six, these two ionic species are possible to extract using 30% TBP in a non-polar diluent, like odorless kerosene (OK) or dodecane. And I've shown this figure here, the right side, where you see the Np(IV), how it is extracted as a function of the nitric acid concentration. And Np(VI) extraction also is given, but lower nitric acid concentration, Np(VI) extraction is higher and at higher nitric acid concentration, Np(IV) extraction is higher. So Np(IV) and Np(VI) can be selectively separated from nitric acid solution by 30% TBP and tuning the nitric acid concentration. On the contrary, if you see the Np(V) extraction is much, much less because, Np(V) ionic potential is much lower and also it has the charge little higher than that of M^{2+}. That is why the interaction with TBP is less. Np(V) is very important for carrying out a lot of studies in the environment. The environmental chemistry of neptunium is mostly focused on the Np(V), that is NpO_2^+, which is very, very mobile in the environmental conditions. And a lot of studies in the laboratory can be carried out using NpO_2^+, which is prepared by using sodium nitrite or even by Fe^{3+}.

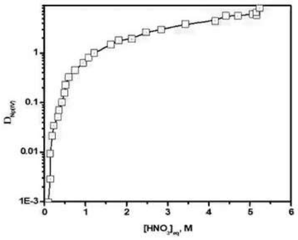
$$Np^{4+} + 4NO_3^- + 2\ TBP \rightarrow Np(NO_3)_4.2TBP$$

Np(IV) in 0.1 HNO_3



Wavelength (nm)	Molar absorptivity
704	53
723	88
961	92
981	36

Radiochim. Acta, I. May et al. (1998)



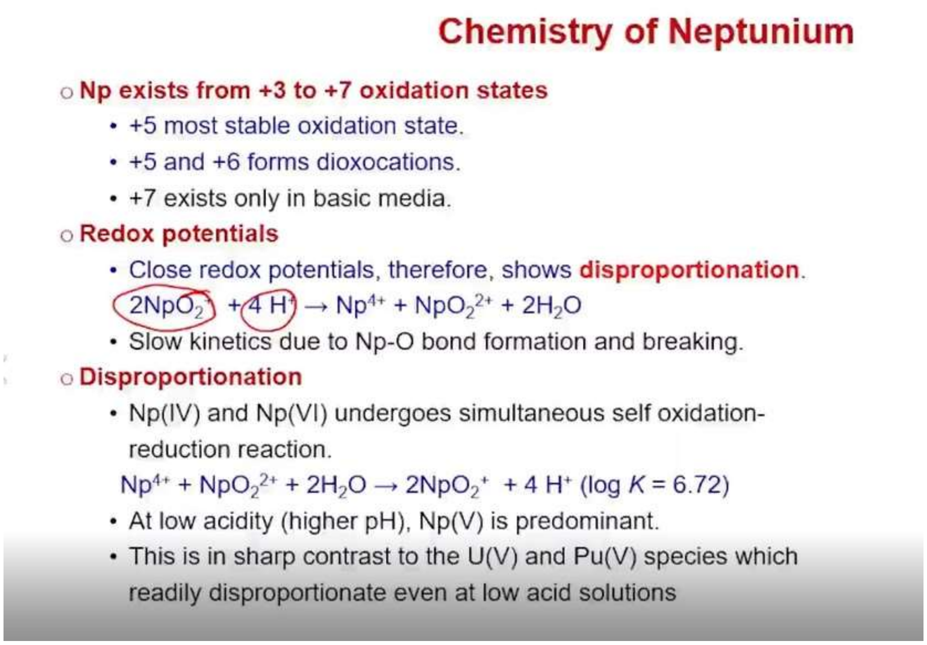
Np(IV) extraction into 30%TBP/OK

Np(IV) is a weaker acid as compared to U(IV) and Pu(IV) and hence, can be stable at 0.1 M HNO_3 but gets hydrolyzed at 0.01 M HNO_3

Wavelength (nm)	Molar absorptivity
703	39
729	36
820	26
845	26
989	26

TBP extract of Np(IV) using 30% TBP/OK

Now this neptunium, TBP, whatever I have shown the extraction, it forms this extraction equilibrium is operative. That means one Np^{4+} ion with four nitrate ions and two TBP. That is, Np(IV) in the aqueous phase, the nitrate ions are also in the aqueous phase, the TBP is in the organic phase and this is $Np(NO_3)_4.2TBP$. This goes to the organic phase. So that is how the extraction is done. Now this, how it is detected, because if it is converted to Np^{4+}, then we can detect by spectrophotometry. There are very characteristic peaks of Np^{4+} and this one peak is there at 704 nanometer as shown in this extreme left table. And another peak is there at 961 nanometer. So these are the two peaks characteristic of Np^{4+}. And then as shown that profile of this Np^{4+} extraction is shown as a function of nitric acid concentration. And this extract spectra, UV-visible spectrophotometry is done. Then you get the 704 nm peak is slightly shifted to 703 nm and this suggests that Np^{4+} is present in the organic phase. Np(IV) is relatively weaker acid as compared to both U(IV) and Pu(IV). Hence, the hydrolysis chance of Np^{4+} in the aqueous medium is relatively lower. And you can find Np^{4+} being stable even at 0.1 molar nitric acid. But if you go to the nitric acid concentration, it gets hydrolyzed. For example, at 0.01 molar nitric acid concentration, Np^{4+} gets hydrolyzed, (forms) hydroxy species. On the other hand, if you want to work with the Pu(IV) and U(IV) ions, that is the Pu^{4+} and the U^{4+} ions, then (in) 0.1 molar nitric acid also they get hydrolyzed. So, for safer side, we go for 0.5 molar nitric acid to carry out the studies of U^{4+} and Pu^{4+}.



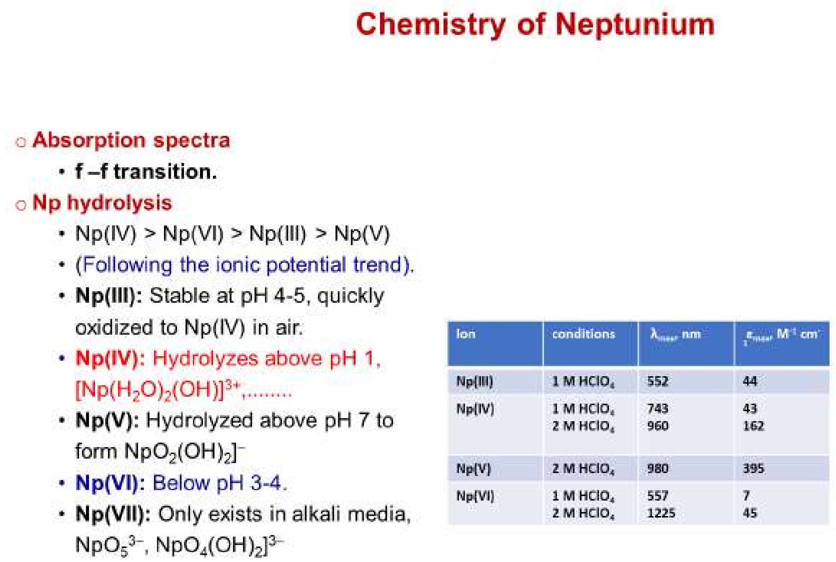
Chemistry of Neptunium

- **Np exists from +3 to +7 oxidation states**
  - +5 most stable oxidation state.
  - +5 and +6 forms dioxocations.
  - +7 exists only in basic media.
- **Redox potentials**
  - Close redox potentials, therefore, shows **disproportionation**.

    $2NpO_2^+ + 4H^+ \rightarrow Np^{4+} + NpO_2^{2+} + 2H_2O$
  - Slow kinetics due to Np-O bond formation and breaking.
- **Disproportionation**
  - Np(IV) and Np(VI) undergoes simultaneous self oxidation-reduction reaction.

    $Np^{4+} + NpO_2^{2+} + 2H_2O \rightarrow 2NpO_2^+ + 4H^+$ (log $K = 6.72$)
  - At low acidity (higher pH), Np(V) is predominant.
  - This is in sharp contrast to the U(V) and Pu(V) species which readily disproportionate even at low acid solutions

Continuing the chemistry of neptunium, as I already mentioned, (in case of) neptunium, the interest is in the neptunyl ion in the plus five oxidation state (NpO_2^+), which is also the most stable oxidation state of neptunium. And (in) +5 and +6 oxidation states, they are forming dioxocations. +7 oxidation state (is) actually only in the basic medium. And Np(V) ions, they are actually undergoing disproportionation. That is, as I have shown here, two NpO_2^+ ions in the presence of strong acid conditions, they disproportionate, i.e., one of them becoming Np^{4+} ion and the second ion is becoming NpO_2^{2+} ion. And that is how this disproportionation reaction is taking place. It has an equilibrium constant of minus 6.72. This is a slow kinetics of this disproportion reaction due to the Np-O bond formation and breaking; in one case actually we are finding (the) one of the NpO_2^+ ion is getting converted to NpO_2^{2+}. So, this is not a slow process. But the NpO_2^+ ion converted to Np^{4+} is a slow process because that is a neptunium oxygen bond breaking is involved in this process. Also, there are other disproportionation reactions like neptunium four and neptunium six. They undergo simultaneous self-oxidation reduction reaction as the reaction is given here. And this is just the opposite of this equilibrium reaction I have given at the top, which is a disproportion reaction of Np(V). And at low acidity, that is at higher pH, neptunium five is dominant and we can carry out studies without bothering much about its stability. This is in sharp contrast to the U(V) and Pu(V) species, which readily disproportionate even at low acid solutions.

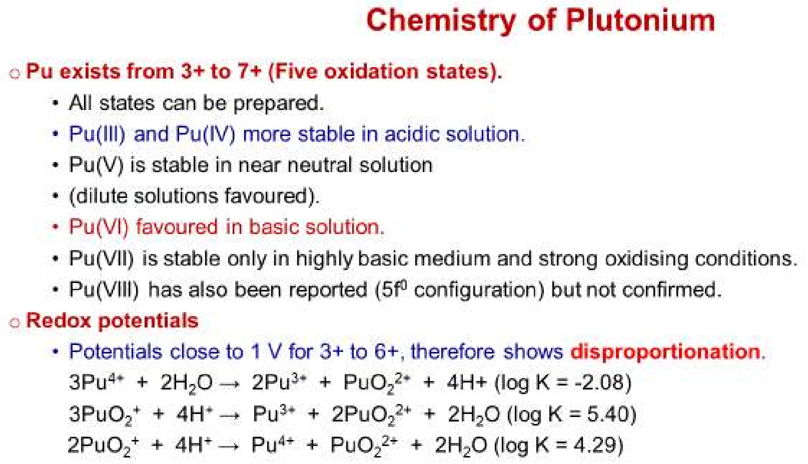


Chemistry of Neptunium

- **Absorption spectra**
  - **f –f transition.**
- **Np hydrolysis**
  - Np(IV) > Np(VI) > Np(III) > Np(V)
  - (Following the ionic potential trend).
  - **Np(III):** Stable at pH 4-5, quickly oxidized to Np(IV) in air.
  - **Np(IV):** Hydrolyzes above pH 1, $[Np(H_2O)_2(OH)]^{3+}$,........
  - **Np(V):** Hydrolyzed above pH 7 to form $NpO_2(OH)_2]^-$
  - **Np(VI):** Below pH 3-4.
  - **Np(VII):** Only exists in alkali media, NpO_5^{3-}, $NpO_4(OH)_2]^{3-}$

Ion	conditions	λ_{max}, nm	ε_{max}, M^{-1} cm^{-1}
Np(III)	1 M $HClO_4$	552	44
Np(IV)	1 M $HClO_4$ 2 M $HClO_4$	743 960	43 162
Np(V)	2 M $HClO_4$	980	395
Np(VI)	1 M $HClO_4$ 2 M $HClO_4$	557 1225	7 45

And neptunium hydrolysis trend is neptunium four gets easily hydrolyzed, which is higher than that of neptunium six, that is a neptunium ion, NpO_2^{2+}, which is again higher than that of Np^{3+} and which in turn is higher than the NpO_2^+, that is (the) Np(V) ion. They follow the ionic potential trend of these ions. This Np(III), it is very, very unstable, but it can be made stable at pH four to five under a very, very special condition. Otherwise this gets quickly oxidized to Np(IV) in air. Np(IV), as I mentioned, it gets hydrolyzed very easily and species of the type $Np(H_2O)_2(OH)^{3+}$ type of species are formed. Np(V), this hydrolyzes above pH seven to form species like $NpO_2(OH)_2^-$ type of species. Np(VI), this is stable only below pH three to four, otherwise it gets hydrolyzed and Np(VII) (is stable only) in alkaline medium.



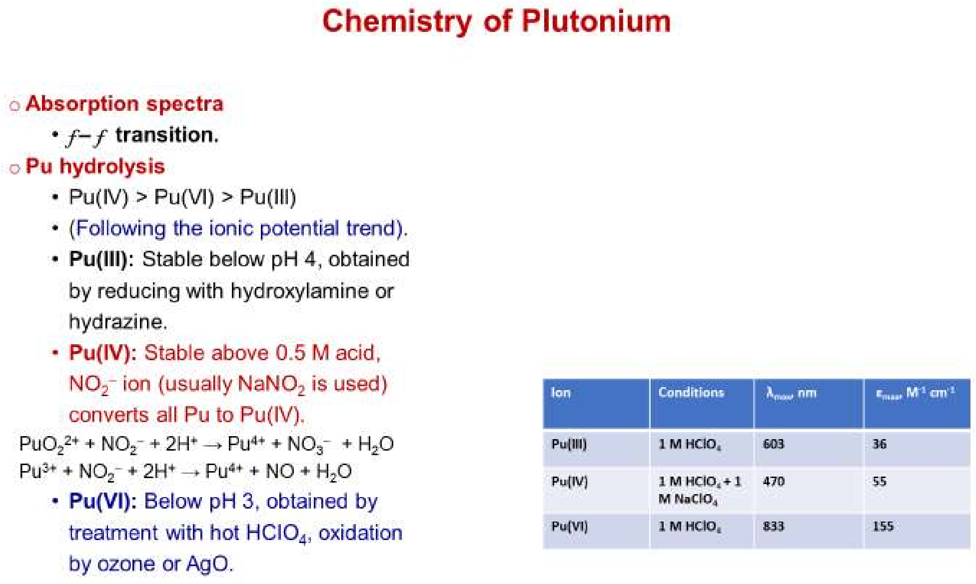
Chemistry of Plutonium

- **Pu exists from 3+ to 7+ (Five oxidation states).**
  - All states can be prepared.
  - Pu(III) and Pu(IV) more stable in acidic solution.
  - Pu(V) is stable in near neutral solution
  - (dilute solutions favoured).
  - Pu(VI) favoured in basic solution.
  - Pu(VII) is stable only in highly basic medium and strong oxidising conditions.
  - Pu(VIII) has also been reported ($5f^0$ configuration) but not confirmed.
- **Redox potentials**
  - Potentials close to 1 V for 3+ to 6+, therefore shows **disproportionation**.

$$3Pu^{4+} + 2H_2O \rightarrow 2Pu^{3+} + PuO_2^{2+} + 4H+ \text{ (log K = -2.08)}$$
$$3PuO_2^{+} + 4H^{+} \rightarrow Pu^{3+} + 2PuO_2^{2+} + 2H_2O \text{ (log K = 5.40)}$$
$$2PuO_2^{+} + 4H^{+} \rightarrow Pu^{4+} + PuO_2^{2+} + 2H_2O \text{ (log K = 4.29)}$$

Now coming to plutonium, it exists from +3 to +7 oxidation states; so, there are five oxidation states. All these oxidation states can be prepared in the laboratory. Pu(III) and

Pu(IV) are more stable in acidic solutions. Pu(V) is stable in near neutral solution, but it disproportionates readily. Therefore, very dilute solutions are favored for Pu(V). Pu(VI) is favored in acidic solutions. Also, Pu(VII) is stable only in highly basic medium and strong oxidizing conditions. Pu(VIII) has been reported but not confirmed. Redox potentials: plutonium potentials (are) close to one volt for all these plutonium oxidation states, this suggests that plutonium undergoes disproptionation. The reactions are given here and see that (from) three Pu^{4+} (ions), Pu^{4+} ions undergo disproptionation giving two Pu^{3+} ions and one Pu(VI), that is PuO_2^{2+} ion and this log K is minus 2.08. Here, (the same) also is the case for the Pu in +5 oxidation state that is PuO_2^{+}, again three of those ions under highly acidic conditions, they give rise to Pu^{3+} and also Pu(VI). Pu(V) also can undergo disproportionation to give one Pu^{4+} ion and one PuO_2^{2+} ion and this has a slightly lower log K values for this equilibrium that is 4.29. This suggests that Pu^{4+}, and Pu(V) that is PuO_2^{+} plus ions can be easily undergoing disproptionation under the laboratory conditions.



Chemistry of Plutonium

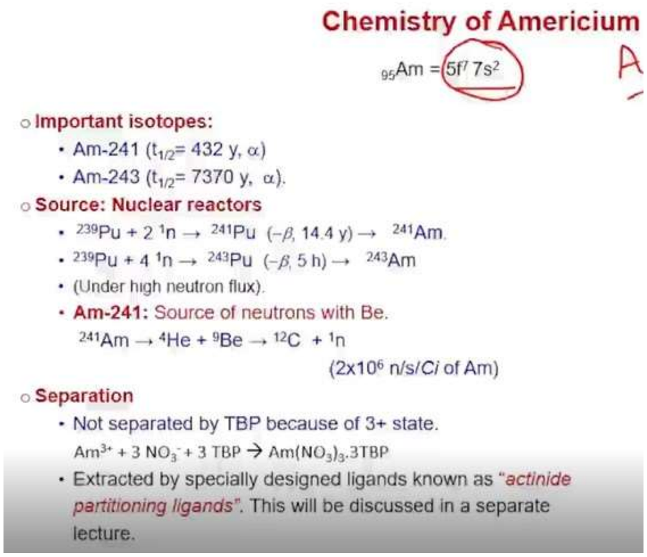
- **Absorption spectra**
  - **$f-f$ transition.**
- **Pu hydrolysis**
  - Pu(IV) > Pu(VI) > Pu(III)
  - (Following the ionic potential trend).
  - **Pu(III):** Stable below pH 4, obtained by reducing with hydroxylamine or hydrazine.
  - **Pu(IV):** Stable above 0.5 M acid, NO_2^- ion (usually $NaNO_2$ is used) converts all Pu to Pu(IV).

$PuO_2^{2+} + NO_2^- + 2H^+ \rightarrow Pu^{4+} + NO_3^- + H_2O$
$Pu^{3+} + NO_2^- + 2H^+ \rightarrow Pu^{4+} + NO + H_2O$

  - **Pu(VI):** Below pH 3, obtained by treatment with hot $HClO_4$, oxidation by ozone or AgO.

Ion	Conditions	λ_{max}, nm	ε_{max}, M^{-1} cm^{-1}
Pu(III)	1 M $HClO_4$	603	36
Pu(IV)	1 M $HClO_4$ + 1 M $NaClO_4$	470	55
Pu(VI)	1 M $HClO_4$	833	155

The absorption spectra of plutonium will be taken up in a separate lecture. Hydrolysis of plutonium: (Hydrolysis of) Pu(IV) is greater than that of Pu(VI) which is greater than that of Pu(III) and this follows the ionic potential trend and Pu(III) is stable below pH four and it is obtained by reducing with hydroxyl amine hydrochloride or hydrazine. Pu(IV) is stable above 0.5 M acid and Pu(IV) is produced by the nitrite ions usually by $NaNO_2$ which is used which converts all the Pu from +3 to +4 state and also from +6 to +4 state. So nitrite has a unique role of oxidizing Pu(III) to Pu(IV) and also reducing Pu(VI) to Pu(IV). And Pu(VI) production can be done below pH three by treatment with hot boiling $HClO_4$ or by oxidation by silver oxide or ozone.



Chemistry of Americium

$_{95}Am = 5f^7\,7s^2$

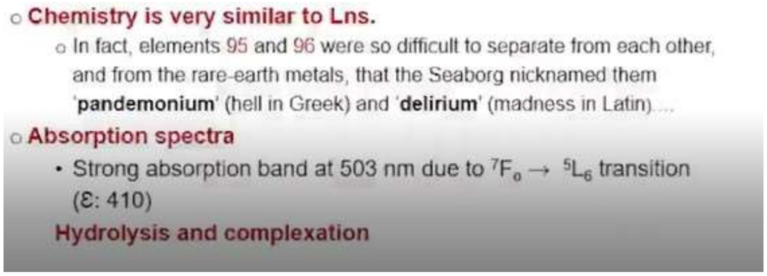
A

- **Important isotopes:**
  - Am-241 ($t_{1/2}$= 432 y, α)
  - Am-243 ($t_{1/2}$= 7370 y, α).
- **Source: Nuclear reactors**
  - $^{239}Pu + 2\,^1n \rightarrow {}^{241}Pu\ (-\beta, 14.4\ y) \rightarrow {}^{241}Am$.
  - $^{239}Pu + 4\,^1n \rightarrow {}^{243}Pu\ (-\beta, 5\ h) \rightarrow {}^{243}Am$
  - (Under high neutron flux).
  - **Am-241:** Source of neutrons with Be.

    $^{241}Am \rightarrow {}^4He + {}^9Be \rightarrow {}^{12}C + {}^1n$

    (2×10^6 n/s/*Ci* of Am)
- **Separation**
  - Not separated by TBP because of 3+ state.

    $Am^{3+} + 3\,NO_3^- + 3\,TBP \rightarrow Am(NO_3)_3.3TBP$
  - Extracted by specially designed ligands known as "*actinide partitioning ligands*". This will be discussed in a separate lecture.



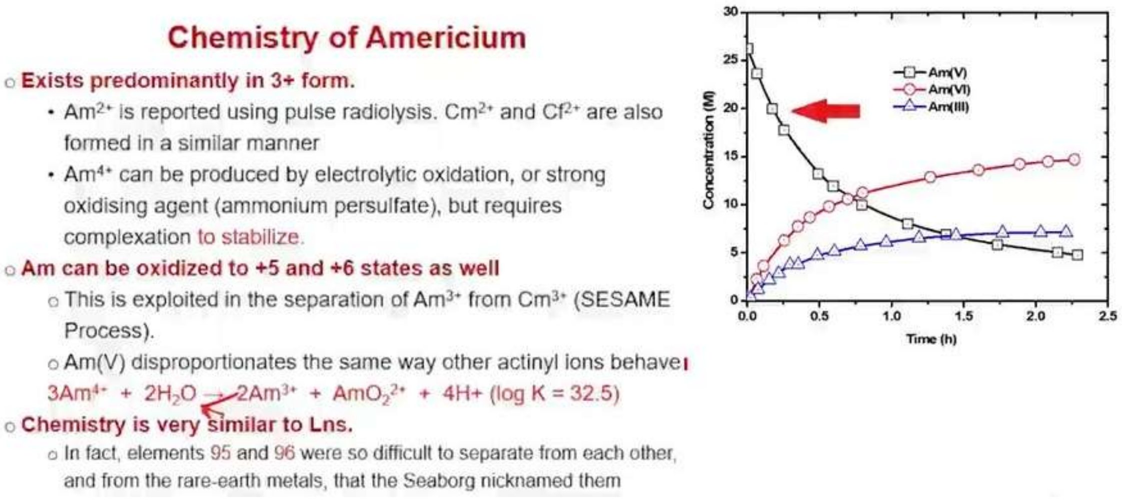
- **Chemistry is very similar to Lns.**
  - In fact, elements 95 and 96 were so difficult to separate from each other, and from the rare-earth metals, that the Seaborg nicknamed them '**pandemonium**' (hell in Greek) and '**delirium**' (madness in Latin)….
- **Absorption spectra**
  - Strong absorption band at 503 nm due to $^7F_0 \rightarrow {}^5L_6$ transition (ε: 410)

Hydrolysis and complexation

Coming to americium, we know this americium oxidation state mostly common is the +3 oxidation state and this is based on this electronic configuration $5f^7$, $7s^2$. One would expect that americium should be stable in the +2 oxidation state as well because you have the $5f^7$ electronic configuration, however, Am^{2+} is not commonly existing in the aqueous solutions and in very rare cases in solids only you can find Am(II). Important isotopes of americium are ^{241}Am, with the half-life of 432 years and it is alpha emitter. It also has a characteristic 60 keV gamma ray. Americium-243 has a half-life of 7370 years. Used mostly for studies where this radiolysis possibilities are to be lesser than that of americium-241. Source of americium is already discussed, so I will not mention it further. Americium-241, which is used as a neutron source along with beryllium, which is called 'americium-beryllium source'. The reaction is given here.

$$^{241}Am\ (\alpha) + {}^9Be \rightarrow {}^{12}C + {}^1n$$

Americium separation is very, very important so far the radioactive waste management is concerned. It is not so important in the nuclear fuel reprocessing. The extraction equilibrium for americium extraction by TBP is given here where you have Am^{3+} in the aqueous phase and 3 nitrate again in the aqueous phase. (With) the 3 TBP in the organic phase going to $Am(NO_3)_3.3\ TBP$, which is the species in the organic phase. Under what condition americium can be extracted by TBP? It can be done by using nitrate salts, that means you can have sodium nitrate high concentration without having nitric acid and then under that condition we can extract Am^{3+}.



Chemistry of Americium

- **Exists predominantly in 3+ form.**
  - Am^{2+} is reported using pulse radiolysis. Cm^{2+} and Cf^{2+} are also formed in a similar manner
  - Am^{4+} can be produced by electrolytic oxidation, or strong oxidising agent (ammonium persulfate), but requires complexation to stabilize.
- **Am can be oxidized to +5 and +6 states as well**
  - This is exploited in the separation of Am^{3+} from Cm^{3+} (SESAME Process).
  - Am(V) disproportionates the same way other actinyl ions behave

$3Am^{4+} + 2H_2O \rightarrow 2Am^{3+} + AmO_2^{2+} + 4H+$ (log K = 32.5)

- **Chemistry is very similar to Lns.**
  - In fact, elements 95 and 96 were so difficult to separate from each other, and from the rare-earth metals, that the Seaborg nicknamed them

Coming to the chemistry of americium ionic species, americium is mostly present in the +3 oxidation state. +2 oxidation state also is reported using some of the pulse radiolysis studies where Am^{2+} is produced, but it is not very stable. Cm^{2+} and Cf^{2+} are also formed in a similar manner. Am^{4+} is again an unusual oxidation state of americium and it can be produced by electrolytic oxidation or strong oxidizing agent like ammonium persulfate, but requires complexation to (get) stabilized. Amiricium can be oxidized to the +5 as well as +6 oxidation states where you get species like AmO_2^+ for the +5 oxidation state and AmO_2^{2+} for the +6 oxidation state and this oxidation of americium to the + 6 oxidation state is exploited for the separation of americium from curium in a process called SESAME process which will be discussed in a subsequent lecture. Am(V) that is AmO_2^+ disproportionates in the same way as other actinyl ions like neptunium, Uranium and plutonium in their pentavalent states in aqueous medium they behave. Also, Am^{4+} undergoes disproportionation (as) I have mentioned here (Fig). Thus, 3 (units of) Am^{4+} + $2H_2O$ giving $2Am^{3+}$ and AmO_2^+. As shown in the lower figure, this disproportionation of amiricium from 6 molar HClO4 is given here where you find that the profile of Am(V) is slowly decreasing and after 2 hours you can see that it becomes almost one third, less than one third that we started with and you have this growing profiles of Am(VI) as well as Am(III). Now coming to the chemistry of americium in the trivalent state, it is very similar to that of lanthanides. We find that this americium creates lot of problem in the radioactive waste management because of the similarity to the trivalent lanthanides. So, lanthanide-actinide separation is one of the very important steps in the radioactive waste management. Also, this americium chemistry is very similar to that of curium and so it was really, really very difficult to separate and that is how Seaborg faced lots of problems in the separation of americium and curium during their discovery. The absorption spectra of americium, the strong absorption band, they have shown here at 503 nm. This characteristic of Am^{3+} is due to the transition to $^7F_0$-->$^5L_6$ transition with an epsilon value of 400. The hydrolysis and complexation of americium will be taken up in a subsequent lecture. Thank you.

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