

# Department Of Chemistry

Udai Pratap Autonomous college Varanasi



Class :- B.Sc.

Semester V<sup>th</sup>

Topic :- Chemistry of Actinides

Sub Title:- Introduction, Electronic configuration and Oxidation states ,magnetic properties, colour and Electronic spectra, Complex formation, Separation of Actinides.

by

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UNIT – 7

CHEMISTRY OF ACTINIDES

- **5f block** elements are called Actinides.
- Chemistry of Actinides are less diverse than that of Lanthanides due their radioactive nature. Element after Uranium is manmade and they are also called Trans Uranium elements.
- Due to more expansion of 5f orbital there is similarity in energies of 5f and 6d orbitals, it means 5f and 6d orbitals are very close. The bond energy is greater than the promotion energy  $5f \longrightarrow 6d$ . The 7S and 7P orbitals are of comparable energy.
- Due to which 6d orbitals also have electron along with 5f orbitals.
- Due to more expansion of 5f orbitals there is more number of electron can removed from this orbital hence more number of oxidation states.
- In case of lighter members due to more similarity in energy of 5f and 6d orbitals more number of electrons can be removed thus higher oxidation state is more stable.
- In case of heavier members +3 oxidation is more common and +2 oxidation state is stable for Nobelium.

### Electronic Configuration and Oxidation States:-

Atomic number	Element	Symbol	Outer Electronic structure	Oxidation states
89	Actinium	Ac	$6d^1 7s^2$	<b>+3</b>
90	Thorium	Th	$6d^2 7s^2$	+3, <b>+4</b>
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	+3, +4, <b>+5</b>
92	Uranium	U	$5f^3 6d^1 7s^2$	+3, +4, +5, <b>+6</b>
93	Neptunium	Np	$5f^4 6d^1 7s^2$	+3, +4, <b>+5</b> , +6, +7
94	Plutonium	Pu	$5f^6 7s^2$	+3, <b>+4</b> , +5, +6, +7
95	Americium	Am	$5f^7 7s^2$	<b>+2</b> , <b>+3</b> , +4, +5, +6
96	Curium	Cm	$5f^7 6d^1 7s^2$	<b>+3</b> , +4
97	Berkelium	Bk	$5f^9 7s^2$	<b>+3</b> , +4
98	Californium	Cf	$5f^{10} 7s^2$	+2, <b>+3</b>
99	Einsteinium	Es	$5f^{11} 7s^2$	+2, <b>+3</b>
100	Fermium	Fm	$5f^{12} 7s^2$	+2, <b>+3</b>
101	Mendelevium	Md	$5f^{13} 7s^2$	+2, <b>+3</b>
102	Nobelium	No	$5f^{14} 7s^2$	<b>+2</b> , +3
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	<b>+3</b>
104	Rutherfordium	Rf	$5f^{14} 6d^2 7s^2$	

**Note:-** The most important oxidation states are shown by bold characters . Other well characterised but less important states are shown by normal letter.

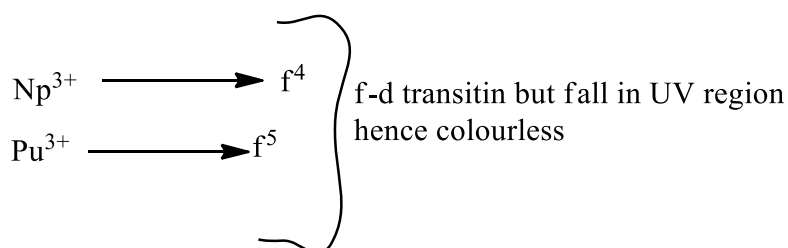
- The +2 state is quite rare.  $Am^{2+}$  has an  $f^7$  configuration. It is the analogue to  $Eu^{2+}$  in lanthanides , but it only exists in the solid as the fluoride .  $Cf^{2+}$ ,  $Es^{2+}$ ,  $Fm^{2+}$ ,  $Md^{2+}$  and  $No^{2+}$  exist as ions in solution. These properties are like the group -2 metals particularly  $Ba^{2+}$  .
- Berkelium in +4 oxidation state is strong oxidising but is more stable than **Curium** and **Americium** due to  $f^7$  configuration.

- When the oxidation states of an actinides increases to +6, the ion is no longer simple ion. There is high charge density on the ion which lead to formation of oxygenated ion eg.  $\text{UO}_2^{2+}$ . Such oxycations are stable in acid and aqueous solutions.

### Colours of Ions and Spectra :-

Actinides ions are generally coloured. The colours of actinides ions depends upon the number of f- electrons. The ions containing no 5f – electrons or seven 5f electrons are colourless.

$\text{U}^{3+} \longrightarrow \text{f}^3$  it show  $\text{f}^3 \text{ d}^1$  s after f-d transition we get  $\text{f}^2 \text{ d}^1$  s third thus it is coloured (red)



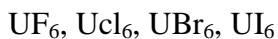
- Here f-f transition also be takes place thus coloured.
- Colour of Actinides is due to charge f-d transition and f-f transition.
- Light member, higher oxidation state compounds are colour due to LMCT.
- In +3 oxidation state some ions have intense colour due to f-d transition, while in case of heavier member, colour is due to f-f transition.
- Absorption peaks of  $\text{Ac}^{3+}$  complexes are broader than that of  $\text{Ln}^{3+}$  complexes this is due to more expansion of 5f orbital than 4f- orbital.
- Intensity of colour of  $\text{Ac}^{3+}$  complexes is more than that of  $\text{Ln}^{3+}$  complexes. This is due to more interaction of 5f- orbital with ligands.
- There is more similarity in absorption spectrum of heavier actinides and lanthanides as compare to that of lighter actinides.

### Magnetic Properties :-

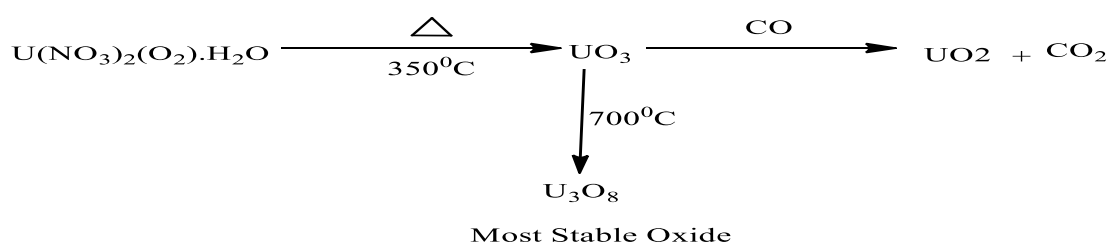
- In case of actinides there is strong spin orbital coupling as well as some quenching of orbital contribution. Thus magnetic moments of actinides are smaller than the theoretical values.
- Quenching of orbital is due to more expansion of 5f orbital with ligands.
- For this reason there is no accurate formula for magnetic moment calculation.
- Among Lanthanides and actinides having same number of unpaired electron suggests more value of magnetic moment for lanthanides.

### Complex Formation Tendency of Actinides. :-

- Complex formation tendency of actinides are better than Lanthanides.
- Chemistry of Thorium and Uranium are well known.
- Thorium preferred to form more stable complexes in +4 oxidation states. It form compounds like halides, oxides, acetate, nitrates etc.
- Uranium form more number of compounds as compared to that of Thorium. This is due to more number of oxidation states of Uranium.



$\text{UF}_6$  is used for enrichment of  $^{235}\text{U}$ . This is due to its higher volatility and single isotope for F. U also forms many oxides in different oxidation states.



Uranium also form  $\text{UO}_2^{2+}$  (Uranyl cation), having linear geometry.  $[\text{O}=\text{U}=\text{O}]^{2+}$ .

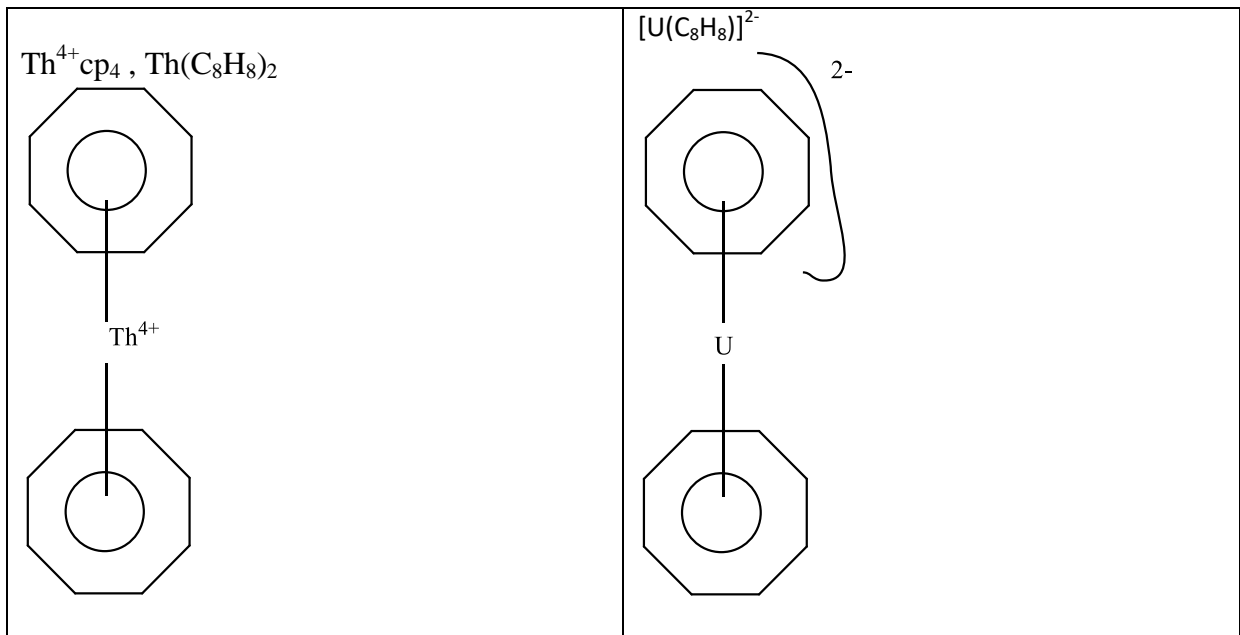
Uranium Cation react with different ligands to form different complexes having linear  $\text{UO}_2$  moiety.

S.No.	Complex	Coordination number	Geometry
1	$[\text{UO}_2(\text{NO}_3)_3]^-$	8	Hexagonal bipyramidal
2	$[\text{UO}_2(\text{NO}_3)_3(\text{H}_2\text{O})_2]^-$	8	Hexagonal bipyramidal
3	$[\text{UO}_2(\text{CH}_3\text{COO})]^-$	8	Hexagonal bipyramidal
4	$[\text{UO}_2(\text{NO}_3)_3(\text{Opph}_3)_2]^-$	8	Hexagonal bipyramidal
5	$[\text{Th}^{4+}(\text{NO}_3)_6]^{2-}$	12	Icosahedral

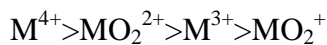
Uranium also formed  $\text{UO}_2^+$  cation but this is less stable than  $\text{UO}_2^{2+}$  and it undergoes disproportionation.



Organometallic chemistry of Th and U are more diverse than that of lanthanides. Like lanthanides they also do not obey 18e- rule.



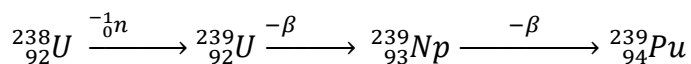
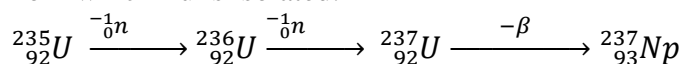
- $\text{UO}_2^{2+}$  forms rather unstable complexes with EDTA as compared to lanthanides.
- With Pyridine,  $\text{ThCl}_4$  as well as  $\text{ThBr}_4$  form monopyridine complexes.
- The degree of complex formation in case of actinides decreases in the order.



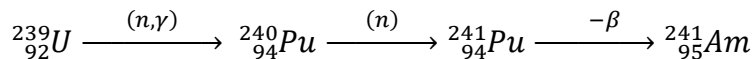
Where M is element of actinides.

### Chemistry of Separation of Neptunium, Plutonium, and Americium from Uranium:-

Although several isotopes of Np, Pu, and Am elements are known yet only few are obtained.  $\text{Np}^{237}$  and  $\text{Pu}^{239}$  are found in the Uranium fuel elements of nuclear reactor from which Pu is isolated.



Americium is formed by succession of  $(n, \gamma)$  reaction starting with plutonium in a nuclear reactor as follows.



The main problem involved in the extraction of these elements includes the recovery of the expensive signatory material and the removal of hazardous fission products that are formed simultaneously.

#### (a) Method based on stability of oxidation states:-

The stability of major ions of these elements involved are  $\text{UO}_2^{2+} > \text{NpO}_2^{2+} > \text{PuO}_2^{2+} > \text{AmO}_2^{2+}$  and  $\text{Am}^{3+} > \text{Pu}^{3+} > \text{Np}^{3+} > \text{U}^{4+}$ . By choosing suitable oxidising

and reducing agent it is possible to obtain a solution containing the element in different oxidation states.

The element can be separated by precipitation or solvent extraction method. Example Pu can be oxidized to  $\text{PuO}_2^{2+}$  whereas Am remains as  $\text{Am}^{3+}$ . Thus  $\text{PuO}_2^{2+}$  can be easily removed by solvent extraction or  $\text{Am}^{3+}$  by precipitation of  $\text{AmF}_3$ .

(b) **Method based on Extraction by using Organic Reagents:-** It is well known fact that  $\text{MO}_2^{2+}$  ions can be extracted from nitrate solution into organic solvents. The  $\text{M}^{4+}$  ions can be extracted from 6M/ $\text{HNO}_3$  solution into tributyl phosphate in kerosene. Similarly  $\text{M}^{3+}$  ions can be separated from 10-16M  $\text{HNO}_3$ .

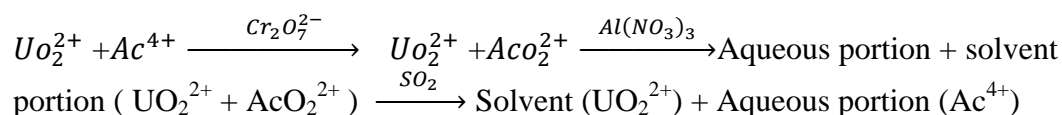
Thus actinides close to each other can be separated by changing the conditions.

(c) **Method based on precipitation:-** In acid solution the actinide  $\text{M}^{3+}$  or  $\text{M}^{4+}$  ions give insoluble fluorides or phosphates. These element in their higher oxidation state are either soluble or can be prevented to get precipitation by complex formation with sulphate or other ions.

(d) **Method based on Ion-Exchange:-** This method is suitable for small amount of material. In this method both cation and anionic ion exchange can be used to separate the actinide ions. The methods are

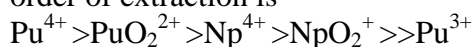
**(1) Isobutyl methyl ketone method:-**

This method used following scheme.



The two layer are separated and collected . Here  $\text{Ac}^{4+} = \text{Np}^{4+}, \text{Pu}^{4+}, \text{Am}^{4+}$ ,

(2) **Tributyl Phosphate Method:-** This method is dependent on the different in extraction coefficient from 6N- $\text{HNO}_3$  into 30% tributyl phosphate in Kerosene. The order of extraction is



And

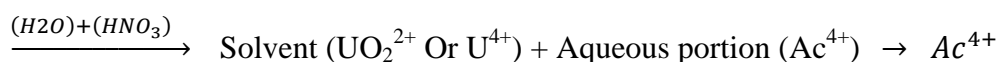


The actinium 3+ ions have very low extraction Coefficient in 6M-  $\text{HNO}_3$  but in 12M-  $\text{HCl}$  or 16M- $\text{HNO}_3$  the extraction increases.

The order of extraction is



The scheme is



Repeat extraction to give  $\text{Ac}^{4+}$  where  $\text{Ac} = \text{Np}$  and  $\text{Pu}$

**(3) Method based on Lanthanum Fluoride cycle:-**

First this method was developed by Np but has found great utility in the separation of Pu from Uranium. (Here solvent is used Kerosene.)

