E-Content

B.Sc. 2nd Year

Inorganic Chemistry Paper-I

UNIT-III

Chapter- 5

PART-II

THE CHEMISTRY OF ACTINIDES

(Transuranic Elements and Their Separations)

Dr. Anil Kumar
Associate Professor
Department of Chemistry,
Harish Chandra P G College,
Maidagin Varanasi, UP-221001
e-mail:anilk642@gmail.com

Transuranic elements

The elements of f-block after uranium, atomic number 93 to 103 (Np-Lr) are called transuranic element. These are all synthesized by nuclear reactions. These elements are radioactive in nature and their half-lives are short period. These elements are also present in uranium in trace quantities.

Synthesis of transuranic elements

The bombardment with neutrons, α-particles or small nuclei like helium and nitrogen by nuclear reaction produced all the transuranic elements. The synthesis route of these elements is shown by the following reactions:

Preparation of neptunium: It was first prepared in 1940 at Berkley (USA) by Seborg, McMillan and Abelson as:

$${}_{92}U^{238} + {}_{0}n^{1} \longrightarrow {}_{92}U^{239} + \gamma \text{ -rays}$$

Now ${}_{92}U^{239}$ due to its unstable nature emits -β particle and produce neptunium

$${}_{92}U^{239} \longrightarrow {}_{93}Np^{239} + {}_{-1}e^{0}$$

Preparation of Plutonium: It was discovered first with decaying -β particle of neptunium by Seaborg as;

$${}_{93}Np^{239} \longrightarrow {}_{94}Pu^{239} + {}_{-1}e^{0} \ (2.42\times10^{4} \text{ years})$$

Preparation of Americium

$${}_{92}U^{238} + {}_{2}He^{4} \longrightarrow {}_{94}Pu^{241} + {}_{0}n^{1}$$

$${}_{94}Pu^{241} \longrightarrow {}_{95}Am^{241} + {}_{-1}e^{0} \ (470 \text{ years})$$

Preparation of Curium: When α-particles bombarded on ${}_{94}Pu^{241}$ curium was prepared.

$${}_{94}Pu^{239} + {}_{2}He^{4} \longrightarrow {}_{96}Cm^{242} + {}_{0}n^{1} \ (162.5 \text{ days})$$

Preparation of Berkelium: Seaborg and his coworkers first prepared Berkelium b bombarding americium with high speed α-particles.

$${}_{95}Am^{241} + {}_{2}He^{4} \longrightarrow {}_{97}Bk^{241} + 2{}_{0}n^{1} \longrightarrow (4.6 \text{ years})$$

Preparation of Californium

$${}_{96}Cm^{242} + {}_{2}He^{4} \longrightarrow {}_{98}Cf^{246} + \gamma \text{ -rays}$$

$${}_{96}Cm^{242} + {}_{2}He^{4} \longrightarrow {}_{98}Cf^{246} + 2{}_{0}n^{1}$$

Preparation of Einsteinium and fermium

$_{92}U^{238} + 17_0n^1 \longrightarrow {}_{92}U^{255}$ + γ-rays

$_{92}U^{255} \longrightarrow {}_{99}Es^{255}$ + γ -rays

$_{92}U^{255} \longrightarrow {}_{100}Fm + 8\ _{-1e0}$

Preparation of Mendelevium and Nobelium

$_{99}Es^{253} + {}_2He^4 \longrightarrow {}_{101}Md^{256} + {}_0n^1$

$_{96}Cm^{246} + {}_6C^{12} \longrightarrow {}_{102}No^{254} + 4_0n^1$ ($t_{1/2}$ =3s)

Preparation of Lawrencium: Lawrencium was prepared by bombarding Californium -250 with accelerated boron nuclei.

$_{98}Cf^{250} + {}_5B^{11} \longrightarrow {}_{103}Lr^{257} + 4_0n^1$ ($1_{1/2}$ = 8s)

Separation of actinide elements: The transuranic elements thus prepared as above are separated from their respective target material and irradiated nuclear fuels by following specialised technique such as ion exchange, carrier precipitation and solvent extraction techniques.

(1) Ion-exchange technique- Modern Technique:

This technique is best and accurate used for quick separation of the actinide ions particularly for small amount of material. However this method shows best use for the separation of the trans-americium elements and also for some of the preceding elements. This method involves the following two steps.

(a) Actinide separated as group-The actinides as a group can be easily separated from the lanthanides by using cation-exchange resin. Eluting agent concentrated HCl is used for elution of column. The actinide ions form chloride complexes more easily and hence are come out first from the column. Now in other method actinides can be separated from lanthanides by using an anion-exchange resin with 10M LiCl as eluting solvent at increasing temperatures upto 90˚C. The elution order shows in their increasing atomic number with the exceptions of Gd, Ho, Cm and Es,. The Lu is absorbed least strongly by column due to bigger size of Lu(aq).

(b) Actinide elements separated individually -

In general actinide ions can be separated individually from each other by using from the cation exchange resin. Elution process is done by eluting solution such as ammonium citrate, lactate, α-hydroxy isobutyrate and ethylene diammine tetra-acetate. Figure P shows the plot of activity against the volume of eluent. Lr (atomic number, Z = 103) is espected to leave the column first, to be followed by No. (Z=102) and so on down the scale of atomic numberswith eluting solvent. Elution positions for Md (Z = 101), Fm (Z = 100) and down to

Am (Z = 95) are shown in this plot. Hear for the comparison of elution curves lanthanide are also shown in the figure- Q. It may be noted that a very close resemblance occurs in the spacing of the corresponding elements in the two series (e.g. Am and Eu, Cm and Gd, Bk and Tb, etc). This feature that make possible for scientists to guess the elution position of the elements from Bk to Md before their discovery and it makes possible today to guess the elution positions of elements with Z = 102 and 103. There is a distinct breakdown found between Gd and Tb (4fseries) and between Cm and Bk (5f-series), which can be ascrved to the small change in ionic radius due to the half filling of the 4f, 5f subshells respectively. The elution order depend on condition and may not be always quite regular as in Fig.

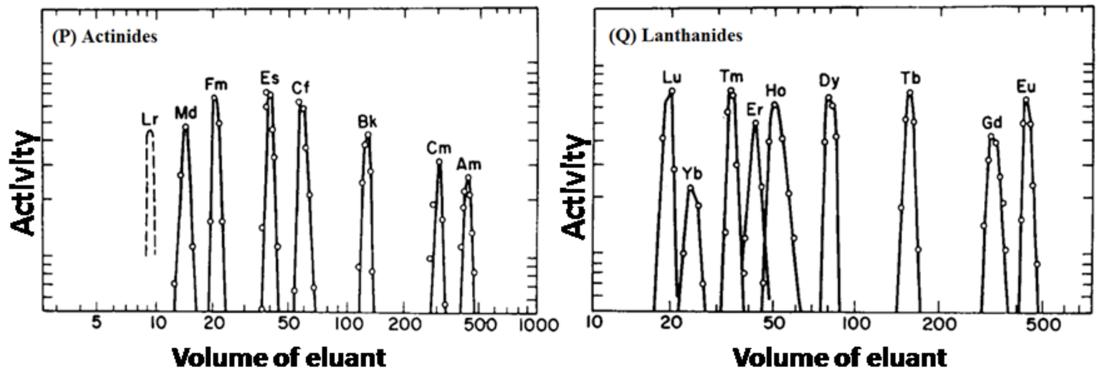


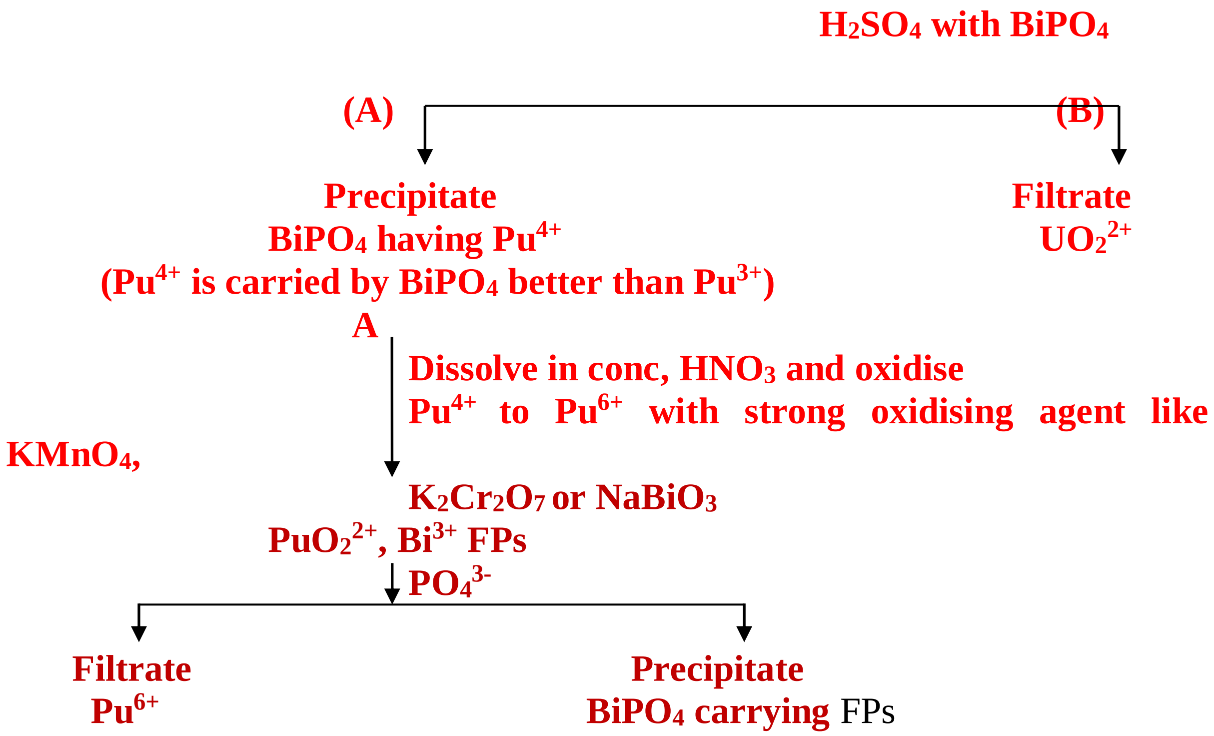
Figure 5.1: Elution curve of Actinides and Lanthanides in their +3 ions.

(2) Precipitation method- This method is used for the tri and tetra positive actinides cations where they can be precipitated in the form of their phosphates or fluorides in acidic solution. Actinides in their higher oxidation states either do not give complexes or form precipitate. When the quantity of the actinide ion is sufficient to precipitate by itself with carrier like $BiPO_4$ or LaF_3 then this method used for the separation of U-Am group element. This method is highly useful and is known as co-precipitation with a carrier like $BiPO_4$ or LaF_3 . Np and Pu that are obtained from spent uranium fuel rod can be separated from uranium and other fission products by applying LaF_3-coprecipitation method. The $BiPO_4$ co-precipitation method widely used in the large scale preparation of Pu from U from fission products was discovered by Thomson and Seaborg . This is shown below:

UO_2^{2+}, Pu^{6+}, fisson products(FP's) $\xrightarrow{NO_2^-}$ **UO_2^{2+}, Pu^{4+}, FPs**

Addition of strong

$\downarrow$

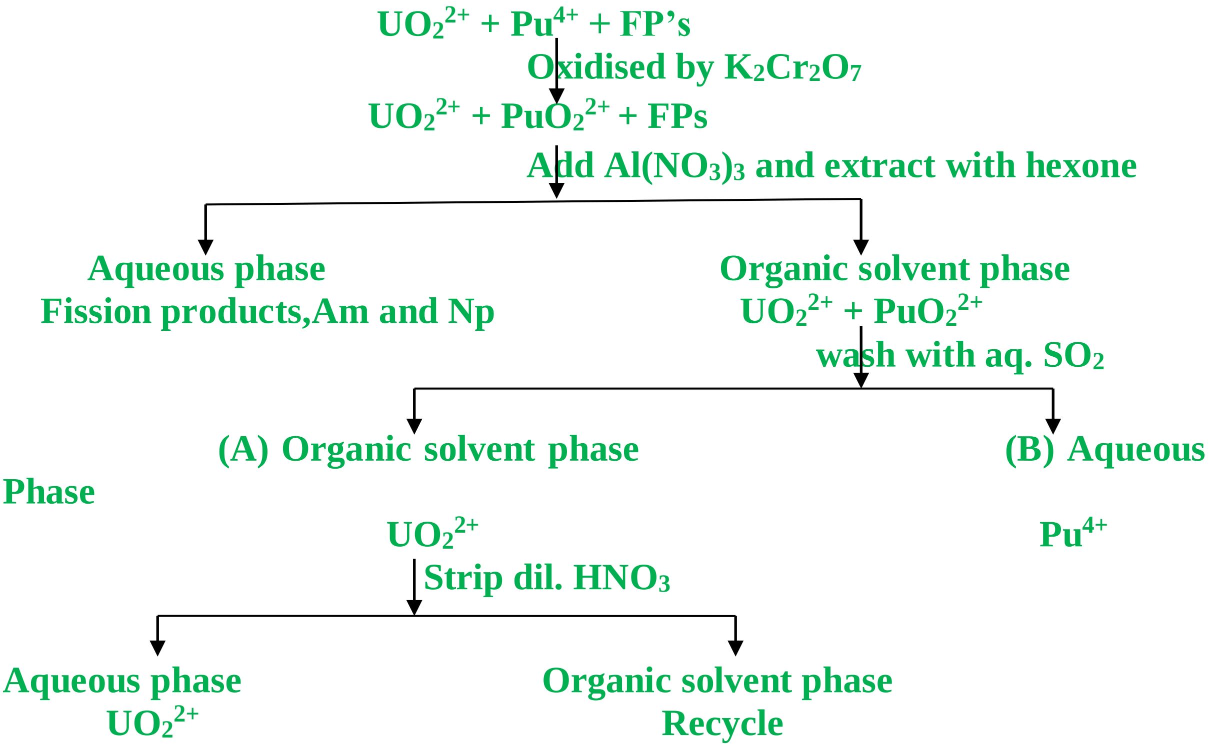


Flowchart for the separation of Pu and U from fission products (FPs) using $BiPO_4$-coprecipitation method.

(3) Solvent extraction method-

The application of this method is extensively depended on the extractability of the actinide elements in their various oxidation states. This technique shows wide applications for the recovery of Pu, Np and Am from U in spent uranium fuel rod removed from the reactor. These are isolated from fission product by solvent extraction method which is based on distribution of metal between the aqueous solution and an organic solvent. Thus we can extract Np^{4+}, Np^{+5}, Pu^{6+} and U^{6+} but we can't extract Pu^{3+} by using methyl isobutyl ketone. Several other solvents such as diethyl ether and tri-n-butyl phosphate (TBP) are also used as extractants. TBP is used as dilute solution of 20% in kerosene due to it's high viscous properties. The ions such as fluoride, sulphate, perchlorate, etc are strongly complexing agent and have tendency to retain the metal in aqueous solution. That's why this method is preferentially applied to nitrate systems. This can be achieved by using $Al(NO_3)_3$ which has a high salt out action. Solvent extraction of Pu and U by hexone and TBP is shown as-

Flowchart-I: Showing separation of Np, Pu , Am and U from spent uranium fuel rod by solvent extraction with methyl isobutyl ketone (hexone) .It is known as Redox process **.**



UO_2^{2+} + Pu^{4+} + FP's

Oxidised by $K_2Cr_2O_7$

UO_2^{2+} + PuO_2^{2+} + FPs

Add $Al(NO_3)_3$ and extract with hexone

Aqueous phase
Fission products,Am and Np

Organic solvent phase
UO_2^{2+} + PuO_2^{2+}

wash with aq. SO_2

(A) Organic solvent phase
UO_2^{2+}

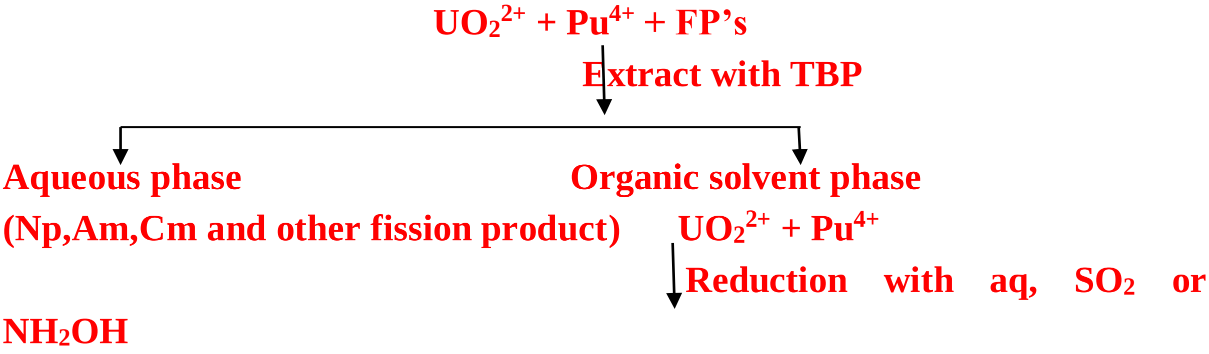
(B) Aqueous Phase
Pu^{4+}

Strip dil. HNO_3

Aqueous phase
UO_2^{2+}

Organic solvent phase
Recycle

Flow chart-II: Separation of Np, Pu , Am and U from spent uranium fuel rod or fission products (FPs) by solvent extraction with tributyl phosphate (TBP), It is known as Purex method.



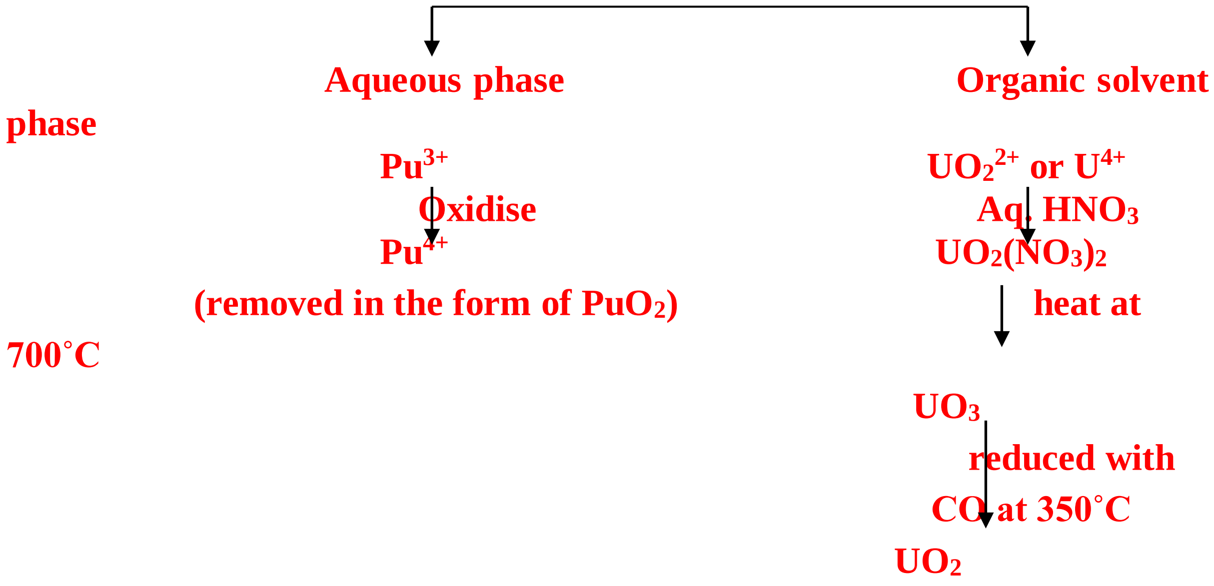
UO_2^{2+} + Pu^{4+} + FP's

Extract with TBP

Aqueous phase
(Np,Am,Cm and other fission product)

Organic solvent phase
UO_2^{2+} + Pu^{4+}

Reduction with aq, SO_2 or NH_2OH



These elements are extracted from spent fuel rods used in nuclear reactor. Their separation is extremely difficult and hazardous. It is because of highly radioactive fission products and material itself also fissile. Pu is highly toxic and carcinogenic.

Differences between Lanthanides and Actinides

1. All Lanthanide elements except promethium are non-radioactive while all actinides are radioactive.

2. In general lanthanides show less number of oxidation states that is in addition to most common oxidation state +3, some of them also show +2 and +4 oxidation state. However actinides show greater number of oxidation state that is in addition to +3, they show +2, +4, +5, +6 and +7 oxidation state.

3. The lanthanides have 4f subshell and the electron enter in 4f–subshell one at each step while actinides have 5f subshell and the electron enter in 5f subshell one by one.

4. Complex formation tendency of lanthanide is less however actinide show greater tendency for complex formation.

5. The compounds of lanthanides are less basic and they do not form oxo-ions while the compounds of actinides are more basic and they form oxo ions such as UO_2^{2+}, PuO_2^{+}, etc.

REFERENCES

1. **Modern Inorganic Chemistry By Prof. R.P. Rastogi, Prof. N.B. Singh and Prof. N.Nath (Publisher- United Book Dept.)**

2. **Advanced Inorganic Chemistry By B.R.Puri,L.R.Sharma and K.C. Kalia (Publisher Milestone-Delhi)**
3. **Advance Inorganic Chemistry Vol.-II By Satya Prakash, G.D.Tuli, S.K.Basu and R.D. Madan(S.Chand)**

4.Chemistry for Degree Students(B.Sc. –IInd year)By Dr. R.L. Madan (S.Chand)

Exercise

Long answer questions

1. Discuss the chemistry of Actinides from the point of view of the following (a) electronic configuration (b) oxidation state (c) magnetic and spectral properties. Indicate how these properties compare with those of Lanthanide elements. (DDU Gorakhpur 1989).

2. What are actinides? Name the various actinides and write down their electronic configuration.

3. Why the electronic configuration of actinides is not definite compared to those of Lanthanides?

4. What is actinide contraction? How will you compare this contraction with that of Lanthanide contraction? Which is more dominating?

5. How will you separate Np, Pu and Am from Uranium? Discuss the basics of separation of these elements from Uranium.

6. Describe separation of Plutonium from Uranium. Write chemical reactions involved in the process. (VBSPU-2010)

7. Discuss the chemistry of separation of Np, Pu and Am from U. (MGKVP-2012)

8. Write the main ores of actinides. How Pu and U are separated from nuclear fission product? (MGKVP-2013)

9. Discuss the chemistry of separation of Np, Pu and Am from Uranium. (MGKVP-2014)

10. What are trans uranic elements? Discuss its properties.

11. How many actinides are found in nature? Which isotope of Uranium is used for atomic energy? What is use of D_2O (Heavy water)? (MGKVP-2015)

12. Describe the method of separation of Np and Pu from Uranium in detail.

Short answer questions

1. Differentiate between the Lanthanide and the actinides.

2. What are transuranic elements? How are they produced?

3. Write a brief account of the oxidation states exhibited by actinide elements and their stabilities.

4. Give a brief account of the chemistry of separation of plutonium from Uranium irradiated in a nuclear reactor. (DDU Gorakhpur-1997)

5. Explain it-

(i) The Later actinides resemble later Lanthanides

(ii) Actinide form oxo cations

(iii) Ions of actinide are coloured

(iv) All the actinide resembles one another very closely

(v) Actinides exhibit higher oxidation state +4, +5, +6 in addition to +3

(vi) Nuclear fuels

6. Discuss Ion exchange method of separation of Actinides.

7. Discuss solvent extraction method of separation of actinides.

8. Give the ray diagram to separate out Plutonium from fission products.

9. Write one nuclear reaction for the synthesis of each elements from neptunium to berkelium. (UP College-2018)

10. Why actinides have greater tendency to form complexes than lanthanides (UP College-2018)

11. Write synthesis of trans uranic elements.

Multiple Choice Questions

1. The elements belonging to 5f-inner transition series are

(a) Th, Pu, Np, Cf, No (b) Sm, Pr, Th, Pu, Np

(c) Pr, Th, Pu, Np, No (d) Sm, Pr, Np, Cf, No

2. Actinide series starts from elements having atomic number from

(a) 89-103 (b) 90-103 (c) 90-104 (d) 91-104

3. The element occurring in nature in trace amount is

(a) neptunium (b) Lawrencium (c) Mendelevium (d) berkelium

4. The first transuranic element is

(a) cerium (b) thorium (c) neptunium (d) berkelium

5. In which class of elements, there is regular filling 5f sub energy level

(a) Lanthanides (b) Transition elements (c) s-block elements (d) actinides

6. Th^{4+} ion is of

(a) yellow colour (b) red colour (c) colourless (d) pink colour

7. The most important oxidation state of Thorium is

(a) +4 (b) +2 (c) +5 (d) +6

8. Which of the following element does not belong to actinides

(a) Cm (b) Th (c) Lr (d) Gd

9. The oxidation state of Uranium in UO_2Cl_2 is

(a) +6 (b) +4 (c) +3 (d) +2

10. Lr^{3+} is

(a) Paramagnetic (b) Diamagnetic

(c) Ferrimagnetic (d) None of these

Answers

1(a) 2(b) 3(a) 4(c) 5(d) 6(c) 7(a) 8(d) 9(a) 10(b)