Actinides

[B] Actinides (5f- Block elements)

Definition: The elements in which the extra electron enters 5f- orbitals of (n-2)th main shall are known as 5f-block elements, actinides or actinones. Thus, according to the definition of actinides only thirteen elements from Th_{90} ($5f^0$ $6d^2$ $7s^2$) to No_{102} ($5f^{14}$ $6d^0$ $7s^2$) should be the members of actinide series. However, all the fifteen elements from Ac_{89} ($5f^0$ $6d^1$ $7s^2$) to Lw_{103} ($5f^{14}$ $6d^1$ $7s^2$) are considered as the members of actinide series, since all these fifteen elements have same physical and chemical properties. In fact actinium is prototype of actinides as lanthanum is the prototype of lanthanides.

General electronic configuration of actinides is 2,8,18, 32, $5s^2$, p^6 d^{10} f^{0-14}, $6s^2$ p^6 d^{0-2}, $7s^2$

- **Electronic configuration of actinides:**

Nos.	**Name**	**At. No. and symbol**	**Electronic configuration**
1	Actinium	Ac_{89}	[Rn] $5f^0$ $6d^1$ $7s^2$
2	Thorium	Th_{90}	[Rn] $5f^0$ $6d^2$ $7s^2$
3	Protactinium	Pa_{91}	[Rn] $5f^2$ $6d^1$ $7s^2$
4	Uranium	U_{92}	[Rn] $5f^3$ $6d^1$ $7s^2$
5	Neptunium	Np_{93}	[Rn] $5f^4$ $6d^1$ $7s^2$
6	Plutonium	Pu_{94}	[Rn] $5f^6$ $6d^0$ $7s^2$
7	Americium	Am_{95}	[Rn] $5f^7$ $6d^0$ $7s^2$
8	Curium	Cm_{96}	[Rn] $5f^7$ $6d^1$ $7s^2$
9	Berkelium	Bk_{97}	[Rn] $5f^9$ $6d^0$ $7s^2$
10	Californium	Cf_{98}	[Rn] $5f^{10}$ $6d^0$ $7s^2$
11	Einstenium	Es_{99}	[Rn] $5f^{11}$ $6d^0$ $7s^2$
12	Fermium	Fm_{100}	[Rn] $5f^{12}$ $6d^0$ $7s^2$
13	Mendelevium	Md_{101}	[Rn] $5f1^3$ $6d^0$ $7s^2$
14	Nobelium	No_{102}	[Rn] $5f^{14}$ $6d^0$ $7s^2$
15	Lawrencium	Lw_{103}	[Rn] $5f^{14}$ $6d^1$ $7s^2$

- **Oxidation states of actinide elements:**

Composition of the oxidation states of lanthanides with those of actinides indicates that +3 oxidation state is most common for both the series of elements. The oxidation state of actinide element is given below:

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
						+2								
+3	-	-	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
	+4	+4	+4	+4	+4	+4	+4	+4						
		+5	+5	+5	+5	+5								
			+6	+6	+6	+6								
				+7	+7									

This oxidation state becomes increasingly more stable as the atomic number increases in the actinide series. The increasing stability of +3 oxidation state is illustrated by the increasing difficulty of oxidation above +3 oxidation state. Actinides show a greater multiplicity of oxidation states. Since in the first half of the actinide series (i.e. lower actinides) the energy required for the conversion 5f→6d is less than that required for the conversion 4f→5d, the lower actinides should show higher oxidation state such as +4, +5, +6 and +7. Correspondingly, since in the second half of the actinide series (i.e. higher actinides), the energy required for the conversion 5f→6d is more than that required for the conversion 4f→5d, and the higher actinides should show more lower oxidation states such as +2.

The tripositive oxidation state occurs widely in each series. The two groups of elements are not entirely comparable in this respect. The +3 state characteristic of lanthanides does not appear in aqueous solution of Th and Pa and this oxidation state become the predominantly stable oxidation state in aqueous solution of the actinides only when we reach Am.

For Th & Pa the +4 & +5 oxidation states are important respectively. From Uranium onward there is very closely related groups U, Np, Pu & Am in which the stability of higher oxidation sate takes place.

The different oxidation states are explained as under:

+2 oxidation state: Only Am (Americium) is known to form a stable +2 state. This state is stable in CaF_2 only and has been studied by optical and electron spin resonance spectra.

+3 oxidation state: +3 state is a general oxidation state for most of the actinides. For Th and Pa +4 and +5 state respectively are important. An^{+4}ions resemble Ln^{+4} ions in their properties. A large number of isomorphous salts are given by the elements of both the series. Trichlorides and trifluorides of Ac, U, Np, Pu and Am are isomorphous. On hydrolysis all the halides give oxyhalides Ac, Pu, and heavier elements give the oxides of An_2O_3 type. Nitrate, perchlorates and sulphates are soluble while hydroxides, fluorides and carbonates are insoluble.

+4 oxidation state: This is the principle oxidation state for Th and is a stable oxidation state up to Am. Am^{+4} and Cm^{+4} exist only as complexes in concentrated fluorides solution of low acidity.
General chemistry of An^{+4}ions is similar to that of Ln^{+4} ions. The hydrated fluorides and phosphates of both An^{+4} and Ln^{+4} ions are insoluble ThO_2, PaO_2, UO_2, NpO_2, AmO_2, CmO_2 and BkO_2 have fluorite structure. The tetrachlorides and tetrabromides of Th, Pa,U and Np are only known, while tetraiodides of Th, U and Np can be prepared by heating AnX_4 with Sb_2O_3. An^{+4} ions from complexes mostly with anionic ligands like HSO_4^-, No_3^-, Cl^- etc.

+5 oxidation state: This state is very important for Pa. Pa^{+5} resemble very much Na^{+5} and Ta^{+5}. U, Np, Pu and Am also exist in +5 oxidation states, but these are less characterized. The only known pentahalides are those of Pa^{+5} and U^{+5}. Fluoro anions of Pa, U, Np and Pu of the types AnF_6^- ' AnF_7^{-2} and AnF_8^{-3} are known to exist in the solid state; AnO_2^+ is the most important ion which contains An^{+5} cation. It has linear structure both in solid and solution.

+6 oxidation state:U, Np, Pu and Am show +6 oxidation state in divalent dioxo cation AnO_2^{+2}. This cation is linear both in solid and solution. The simple molecular halide, UO_2F_2 has the linear O-U-O group with flourine bridges .The O-U bond distance is 1.75 o 2.00 Å. The overall structure is flattened octahedron .Although AnO_2^{+2}cation is linear in shape, it forms complexes with exceptional geometries, e.g. four, five and six co-ordinated complexes are given by this cation.

+7oxidation state: +7 oxidation state is shown only by Np and Pu. Electrolysis or ozone oxidation of Np^{+5} or Np^{+6} in NaOH gives a green solution of NpO_5^{-3} which is slowly reduced to
Np^{+6} at 25^0C.

Actinide Contraction: The shielding of one f-electron by another from the effect of nuclear charge is quite weak on account of the shape of the f- orbital, hence with increasing atomic number, the effective nuclear charge experienced by each 5f-electron increases. This causes shrinkage in the radius of atoms or ions as one proceed from Ac to Lw. This accumulation of successive shrinkage is called actinide contraction.

- **Comparison of Actinide and Lanthanide elements:**

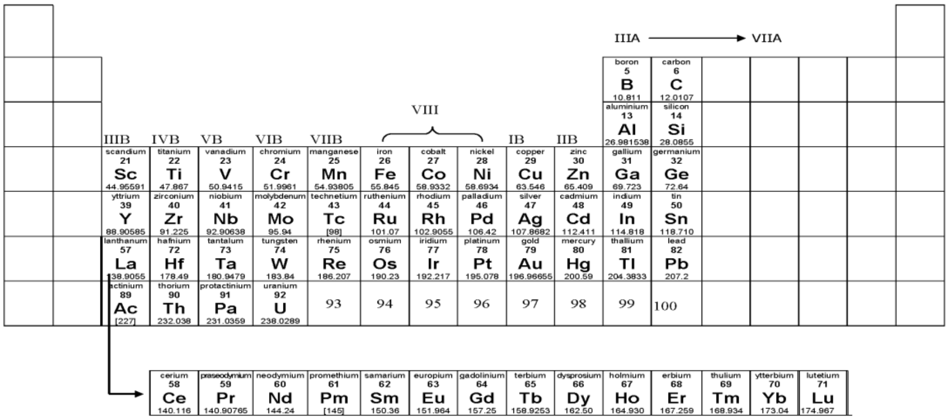
Lanthanides	**Actinides**
1. In lanthanide the newly added electron enters in 4f- orbitals.	1. In actinide the newly added electron enters in 5f- orbitals.
2. The name lanthanide is given because the first element is lanthanum and all the other elements have similar property to that of lanthanum element.	2. The name actinide is given because the first element is actinium and all the other elements have similar property to that of actinium element.
3. They have less binding energy, hence less shielding effect in 4f- orbital.	3. They have more binding energy, hence more shielding effect in 5f- orbital.
4. They have low tendency to form complex. They form complex with ligand having oxygen or oxygen plus nitrogen like glycine, oxalate etc.	4. They have greater tendency to form complex with π-accepter ligand and anions.
5. Their colour absorptive spectra are less intense than actinides.	5. Their colour absorptive spectra are more intense than lanthanides.
6. They have lower ionic radii than actinides.	6. They have greater ionic radii than lanthanides.
7. They have more magnetic moment than the actinides.	7. They have less magnetic moment than the lanthanides.

- **Position of Actinides in the Periodic table:**

The position of actinides can be explained in two ways:

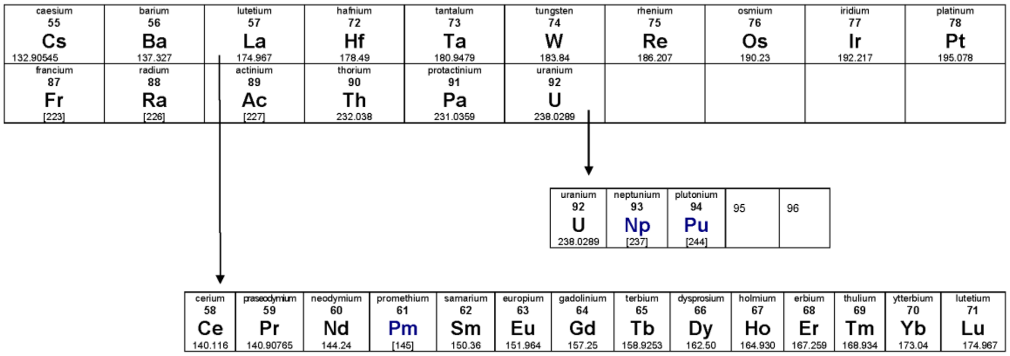
(i) Prior to the discovery of the trans-uranium elements:

Before 1940, the existence of the lanthanide series helped that another series of elements resulting from the addition of the electrons to an (n-2) f- shell (i.e. 5f - shell) should occurs somewhere in the heavy elements region. Prior to the discovery of trans-uranium elements, the naturally occurring heaviest known elements namely Th_{90}, Pa_{91}, and U_{92} where placed below Hf_{72}, Ta_{73}, W_{74} in IV B, V B and VI B groups of the periodic table because these elements showed +4, +5 and +6 oxidation states and resembled Hf, Ta and W respectively in many of their properties. The undiscovered trans-uranium elements with atomic numbers 93 to100 were thus expected to occupy the position in the periodic table below Re_{75}, Os_{76}, Ir_{77}, Pt_{78}, Au_{79}, Hg_{80}, Tl_{81} and Pb_{82} respectively as shown below:



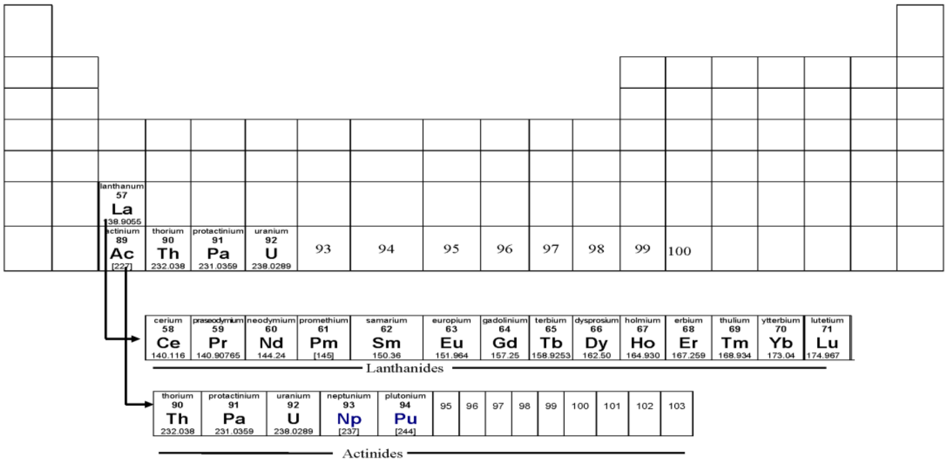
(ii) Following the discovery of the trans-uranium elements:

The discovery of the element neptunium (Np_{93}) came in 1940 and this discovery was followed shortly by the discovery of plutonium (Pu_{94}) in 1941. The tracer chemical experiment with Np_{93} and Pu_{94} showed that the chemical properties of these of Re_{75} and Os_{76}. On this basis in 1944, the position of U_{92}, Np_{93} and Pu_{94} was shown in the periodic table as shown below:



It was thought that the undiscovered elements with atomic numbers 95 and 96 should be very much like U_{92}, Np_{93} and Pu_{94} in their chemical properties. This assumption, however, proved to be wrong, since the experiments directed towards the discovery of elements with atomic numbers 95 and 96 on the pattern of discovery of Np_{93} and Pu_{94} failed. Later on in the same year (1944) Seaborg thought that all the known elements heavier than Ac_{89} were wrongly placed in the periodic table as shown in above figure.

He advanced the idea that the elements having atomic numbers greater than that of Ac_{89} might constitute a second series of inner transition elements similar to the lanthanides series. There elements are called actinide elements. The new position of the actinides was further confirmed by the fact that all the predicted elements up to 130 were discovered by 1961. As shown in figure below:

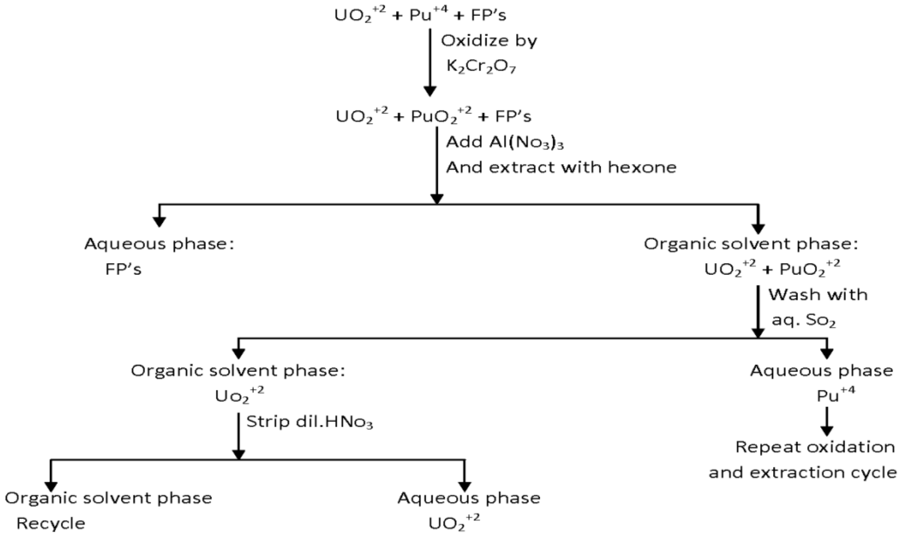


- **Separation of Actinide elements:**

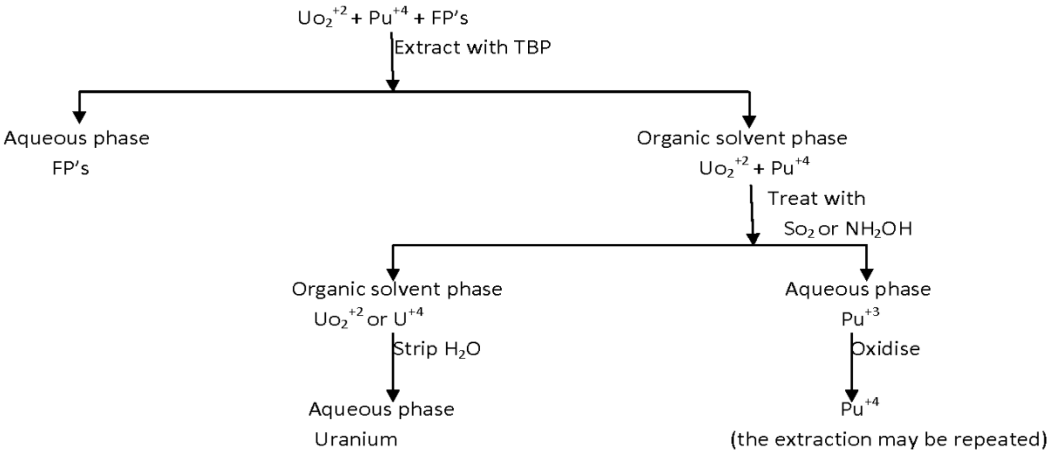
(1) Solvent extraction method:

This method depends on the extractability of the various oxidation state of actinide elements. This technique finds extensive application in the recovery of U and Pu from used – up nuclear fuels. This process is based on the distribution of a metal between the aqueous solution and an organic solvent. Thus with methyl isobutyl ketone (hexone) Np^{+4}, Np^{+5}, Pu^{+6} and U^{+6} are extracted while Pu^{+3} is not extracted. Diethyl ether and tri-n-butyl phosphate (TBP) are other solvent which are used as extractants. Because of the high velocity and density, TBP is used as 20% solution in kerosene. The method is preferentially applied to nitrate system, because other ions like sulphate, perchlorate, fluoride etc are strongly complexing and tend to retain the method in aqueous solution. Hexane and diethyl ether require a high concentration of No_3^- ions in the aqueous phase and it is achieved by adding $Al(No_3)_3$ which has a high salt – out action. TBP is resistant to nitric acid oxidation and acts by itself as a salt agent. Solvent extraction of Pu and U by hexone and TBP is shown below:

(i) Separation of Pu and U from fission products (FP's) by solvent extraction with hexone (Redox process).



(ii) Separation of Pu and U from fission products (FP's) by solvent extraction with tributyl phosphate TBP (Purex process):



(2) **Ion – exchange technique:**

This is the best technique to separate the actinide ions. This method involves the following two steps:

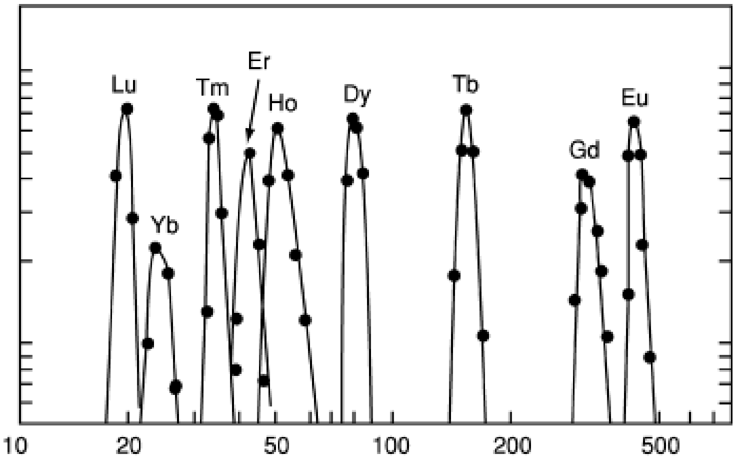
(i) Lanthanide – actinide separation:

The actinide as a group are separated from lanthanides by cation – exchange resin. Strong HCl is used as the eluting agent. The actinide ions from chloride complexes more easily and hence are eluted first.

Separation of actinides from Lanthanides is now done on an anion – exchange resin with 10ml LiCl as eluent at elevaled temperature up to 90^0c with the exceptions of Gd, Ho and of Cm, Es the elution sequences proceed in the order of increasing atomic number. Thus La is absorbed least strongly.

(ii) Separation of individual actinide elements:

The actinide ions can be separated from each other by removing from the cation exchange resin by elution with ammonium citrate, lactate, α-hydrogen isobutyrate and ethylene diamine tetracetate. If the activity is plotted against the number of drops of eluent , elution curves will be obtained as shown below:



Lw (at. no. z = 103) is predicted to leave the column first to be followed by No (z= 102) and so on down the scale of atomic numbers. Elution position for Md (z= 101) Fm (z= 100) and down to Am (z=95) are shown in the typical elution carves elution carves for lanthanides are also shown in figure as under.

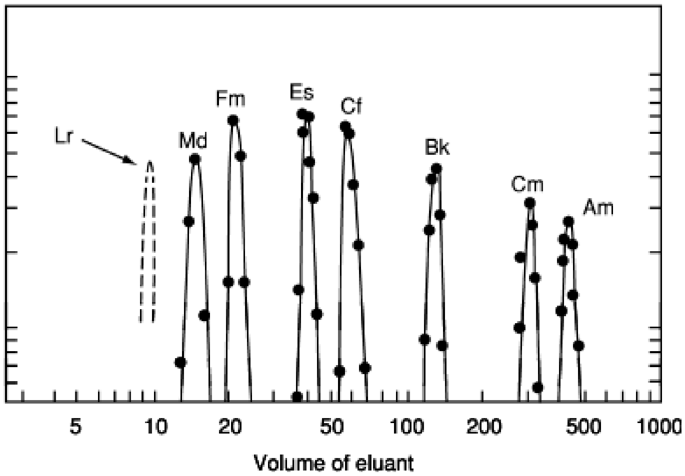


Figure: Elution curves showing the elution positions of Ln^{3+} and An^{3+} ions eluted from Dowex-50 ion-exchange resin with ammonia alpha-hydroxy-isobutyrate. The dotted elution curve indicates the predicted position of the then undiscovered elements with atomic number 102.

It may be noted that a very striking similarity occurs in the spacing of the corresponding elements in the two series (e.g. Am and Eu, Cm and Gd, Bk and Tb etc.). It is similarity that made possible for scientists to predict the elution positions of the elements from Bk_{97} to Md_{101} before their discovery and which also makes possible today to predict the elution position of elements with no (z= 102) and Lw(z = 103).

There is a distinct breakdown between Gd and Tb (Lanthanide series) and between Cm and Bk (actinide series), which can be attributed to the small change in ionic radians made by the half-filling of 4f and 5f shells respectively. The elution order is not always regular as shown in above figure.

- **Color and Absorption spectra of actinide ions:**

Colors and the wavelengths of the more prominent light absorption bands of actinide ions like An^{+3}, An^{+4}, AnO_2^{+} and AnO_2^{+2} are given in table as under.

Table: Color and Wave lengths (in Å) of more prominent light absorption bands of actinide ions.

Elements	***An^{3+} ions***	***An^{4+} ions***	***AnO_2^{+} ions***	***AnO_2^{2+} ions***
Ac	Colorless *($5f^{0}$)*	–	–	–
Th	–	Colorless *($5f^{0}$)*	–	–
Pa	–	Colorless *($5f^{1}$)* (2240,2550,2700)	Colorless	–
U	Red *($5f^{3}$)* (5200,8800,9000)	Green *($5f^{2}$)* (5500, 6500)	–	Yellow (4000, 4110,4250)
Np	Blue or Purple *($5f^{4}$)* (5520, 6610, 7875)	Yellow-Green *($5f^{3}$)* (5040, 7430, 8250)	Green	Pink to Red (4760, 5570)
Pu	Blue or Violet *($5f^{5}$)* (5600, 6000, 6030)	Tan to orange brown *($5f^{4}$)* (4700, 6550, 8150)	Reddish-Purple	Yellow to pink orange (8330, 9530, 9830)
Am	Pink *($5f^{6}$)* (5027, 8200)	Rose *($5f^{7}$)*	Yellow (5131, 7151)	Run-colored (6660, 9950)
Cm	Colorless *($5f^{7}$)* (2368, 2680, 2774)	–	–	–

If may be seen that by comparing the colors of Ln^{+3} and An^{+3} ions the pairs of ions which have the same number of f- electrons (4f and 5f electron) have roughly comparable color. The pairs viz. (i) Nd^{+3} ($4f^{3}$- reddish) and U^{+3} ($5f^{3}$- reddish) and (ii) Gd^{+3} ($4f^{7}$- colorless) and Cm^{+3} ($5f^{7}$ – colorless) illustrate this point. Ce^{+3} ($4f^{1}$) and Pa^{+4}($5f^{1}$) ions are colorless.

The absorption spectra of actinide ions, in aqueous solution and in crystals, contain narrow bands in the visible, near ultraviolet and near infrared regions of the spectrum. The bands seen in case of actinide ions arise from electronic transitions between energy states within the 5f- electron sub- sell. It has been found that the absorption bands seen in case of actinide ions are about ten times sharper than those seen in case of lanthanide ions. The absorption spectra of lanthanide ions are observed due to electronic transitions between energy states within the 4f-electron sub-shell.

Light absorption spectra of lanthanides are much more affected by environment. Charge-transfer phenomena occur more frequently and the bands are more intense in the actinides because of lower energy involved in transitions. Moreover, the overlap of 5f- orbitals with the ligand orbitals increases the intensity of absorptions bands.

- **Magnetic properties of Actinide elements:**

In the 5f-series, Pu^{+3} and Am^{+3} ions show analogous behavior as noted for Sm^{+3} and Eu^{+3} ions in 4f-series. The magnetic properties of the actinides ions are considerably more difficult to explain than those of the lanthanide ions. The values of magnetic moments found experimentally are usually lower than those calculated using russellsaunders coupling scheme. This is due perhaps to the inadequacy of the russellsaunders coupling scheme for $5f^{n}$ ions and also to more soluble ligand field effects which involve 5f-orbitals to a greater extent than the 4f-orbitals are involved in bonding in the lanthanide complexes.

An equation used for the calculation of molar susceptibility X_M is given by,

$$X_M = \frac{Ng^2\beta^2J(J+1)}{3kT} + N\alpha$$

Where N = Avogadro's number, g= lande splitting factor
Which is given by:

$$g = 1 + \frac{S\,(S+1) + J\,(J+1) - L(L-1)}{2J\,(J+1)}$$

$$\beta = \text{Bohr magneton} = \frac{eh}{2\pi mc}$$
$$= 9.27 \times 10^{-21} \text{ erg/gauss}$$

J = Total angular momentums of atom = | L+S|

K = Boltzmann constant, T = absolute temperature and α = small temperature independent term due to second order Zeeman effect.

Strictly speaking the above equation can be applied only to gaseous ions in which the multiplet intervals are larger compound to KT and value of J to be used in it is taken from the ground state symbols of ions.

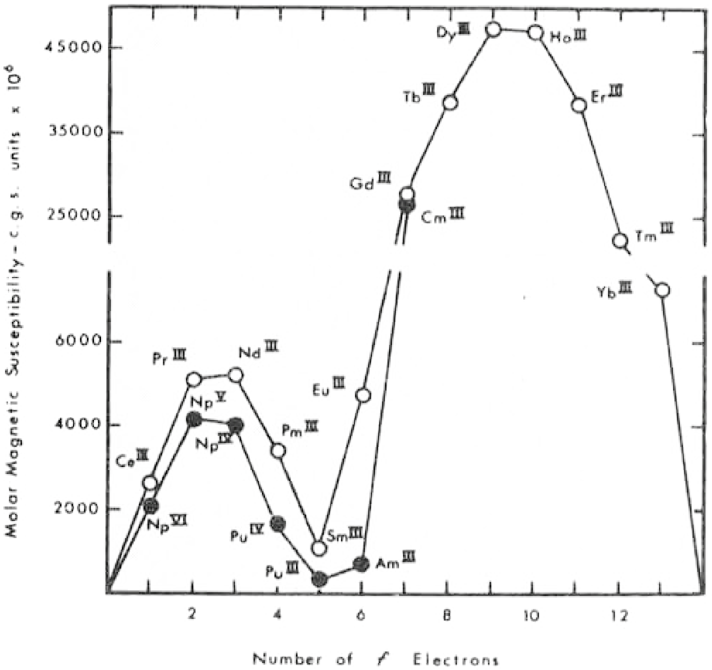


Figure: Comparison of magnetic susceptibility of Lanthanides and Actinides

A comparison of the plots of molar magnetic susceptibilities of tripositive lanthanide and actinide ions against the number of 4f or 5f – electrons (as shown in above figure) reveals that there are remarkable similarities between the two plots. The plot of lanthanide ions has two humps while that of actinide ions has only one. In both the cases the first hump is at the identical place. The moments of the lanthanide ions agree closely with theoretical predictions but those of the transuranic ions are somewhat lower than expected as shown in figure below. This is because the 5f-electons of the transuranic ions are less effectively screened from the crystal field and then are the 4f-electrons of the lanthanide ions.

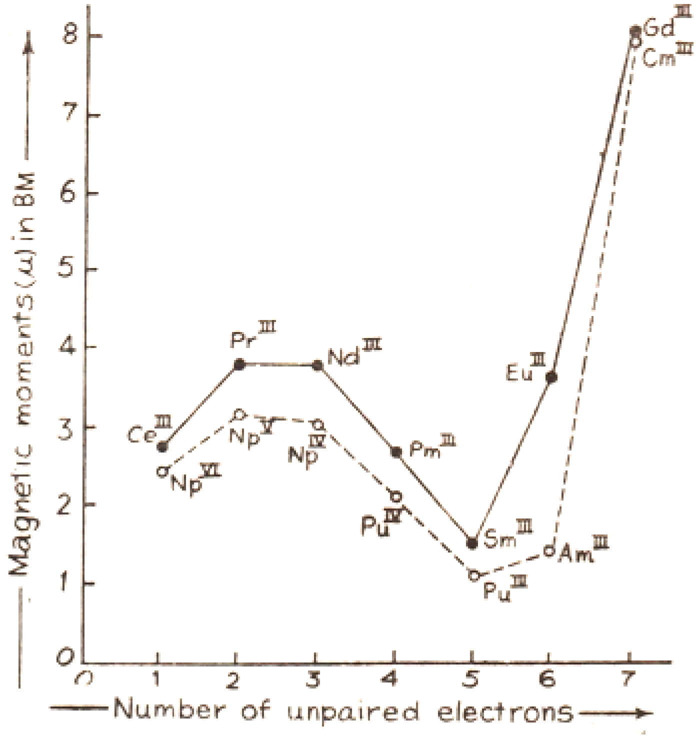


Figure: Comparison of magnetic moments of Lanthanides and Actinides.

- **Complex formation of Actinide elements**

The degree of complex formations decreases in the order:

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

The complexing power of different singly charged and doubly charged anions follows the order:

Singly charged anions: $F^{-} > No_3^{-} > Cl^{-}$

Doubly charged anions: $Co_3^{-2} > Ox^{-2} > So_4^{-2}$

Actinides also form complexes with a large number of organic substances.