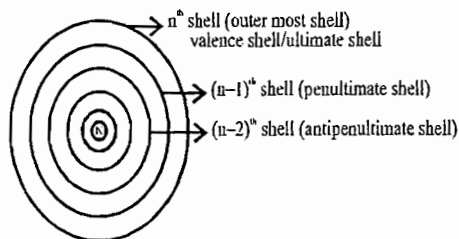


## CHEMISTRY OF LANTHANIDE & ACTINIDE

### (f-block element)



The elements in which the differentiating electron (last electron) enters the antepenultimate i.e.,  $(n-2)f$  energy levels, are called  $f$ -block elements. These elements have also been called inner transition elements because the last electron in these elements enters into  $(n-2)f$ -orbitals i.e., inner to penultimate, earths because these elements were known to be rare. But now this name is not appropriate because many of these elements are not rare.

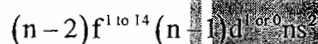
#### Classification of $f$ -block Elements:

- (1) **Lanthanides:** The elements in which the last electron enters one of the  $4f$ -orbitals are called  $4f$ -block elements or first inner transition series. These are also called lanthanides or lanthanons because they come immediately after lanthanum.
- (2) **Actinides:** The elements in which the last electron enters one of the  $5f$ -orbitals are called  $5f$ -block elements or second inner transition series. These are also called actinides or actinons because they come immediately after actinium.

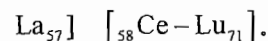
In past they were called rare earth metals.

**Note :** Lanthanum, though a  $d$ -block element, is included in the lanthanide series because it closely resembles lanthanides. Similarly, actinium is also included in the actinide series.

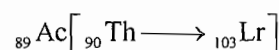
#### General configuration:



Lanthanum is not element of lanthanide series.



Only Pm (Promathium) is radioactive element



Radioactive  
but it is stable  
& found in nature

Highly radioactive man made  
element, synthetic element. They  
don't found in nature

- \* Rare earth metals.
- \* They are highly reactive elements
- \* They are much more reactive than transition metal.
- \* They liberate  $H_2$  gas when reacted with water.
- \* Their reactivity matches with alkaline earth metals especially with Ba.



South Delhi : 28-A/11, Jia Sarai, Near-IIT Hauz Khas, New Delhi-16, Ph : 011-26851008, 26861009

North Delhi : 33-35, Mall Road, G.T.B. Nagar (Opp. Metro Gate No. 3), Delhi-09, Ph: 011-65462244, 65662255

### The Lanthanide Series (4f-block elements)

The general electronic configuration of lanthanides is  $4f^{0-14}, 5d^{0 \text{ or } 1}, 6s^2$ . It might be expected that the 14 elements from cerium to lutetium would be formed by adding 1, 2, 3,.....14 electrons into the 4f level. However, it is energetically favourable to move the single 5d electron into the 4f level in most of the elements, but not in the cases of Ce, Gd and Lu. The reason why Gd has a  $5d^1$  arrangement is that this leaves a half filled 4f level, which gives increased stability. Lu has a  $5d^1$  arrangement because the f shell is already full. The lanthanides are characterized by the uniform (+III) oxidation state shown by all the metals. They typically form compounds which are ionic and trivalent. The electronic structures of the ions are  $Ce^{3+} f^1, Pr^{3+} f^2, Nd^{3+} f^3, \dots, Lu^{3+} f^{14}$ .

The 4f-electrons in the antepenultimate shell are very effectively shielded from their chemical environment outside the atom by the 5s and 5p electrons. Consequently the 4f electrons do not take part in bonding. They are neither removed to produce ions nor do they take any significant part in crystal field stabilization of complexes. Crystal field stabilization is very important with the d-block elements. The octahedral splitting of f orbitals  $D_0$  is only about  $1 \text{ kJ mol}^{-1}$ . Whether the f orbitals are filled or empty has little effect on the normal chemical properties. However, it does affect their spectra and their magnetic properties.

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Lanthanide element:	$4f^{(1-14)} 5d^{1 \text{ or } 0} 6s^2$			
Elements	Atomic Number	Electronic structure of atoms	Electronic str. of $M^{3+}$	
Lanthanum	La 57	$[Xe] 4f^0 5d^1 6s^2$	$4f^0$	
Cerium	Ce 58	$[Xe] 4f^1 5d^1 6s^2$	$4f^1$	
Praseodymium	Pr 59	$[Xe] 4f^3 5d^0 6s^2$	$4f^2$	
Neodymium	Nd 60	$[Xe] 4f^4 5d^0 6s^2$	$4f^3$	
Promethium	Pm 61	$[Xe] 4f^5 5d^0 6s^2$	$4f^4$	
Samarium	Sm 62	$[Xe] 4f^6 5d^0 6s^2$	$4f^5$	
Europium	Eu 63	$[Xe] 4f^7 5d^0 6s^2$	$4f^6$ or $4f^7$	
Gadolinium	Gd 64	$[Xe] 4f^7 5d^1 6s^2$	$4f^6$ (Half filled shell)	
Terbium	Tb 65	$[Xe] 4f^9 5d^0 6s^2$	$4f^8$	
Dysprosium	Dy 66	$[Xe] 4f^{10} 5d^0 6s^2$	$4f^9$	
Holmium	Ho 67	$[Xe] 4f^{11} 5d^0 6s^2$	$4f^{10}$	
Erbium	Er 68	$[Xe] 4f^{12} 5d^0 6s^2$	$4f^{11}$	
Thulium	Tm 69	$[Xe] 4f^{13} 5d^0 6s^2$	$4f^{12}$	
Ytterbium	Yb 70	$[Xe] 4f^{14} 5d^0 6s^2$	$4f^{13}$ or $4f^{14}$	
Lutetium	Lu 71	$[Xe] 4f^{14} 5d^1 6s^2$	$4f^{14}$	

**Oxidation States:** The sum of the first three ionization energies for each element are low. Thus the oxidation state (+III) is ionic and  $Ln^{3+}$  dominates the chemistry of these elements. The  $Ln^{2+}$  and  $Ln^{4+}$  ions that do occur are always less stable than  $Ln^{3+}$  (the symbol Ln is used to denote any of the lanthanides). In just the same way so for other elements, the higher oxidation states occur in the fluorides and oxides, and the lower oxidation states occur in the other halides, particularly bromides and iodides. Oxidation number (+II) and (+IV) do occur, particularly when they lead to:

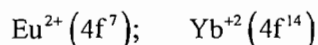
1. A noble gas configuration, e.g.,  $Ce^{4+} (4f^0)$
2. A half filled f shell, e.g.,  $Eu^{2+}$  and  $Tb^{4+} (4f^7)$
3. A completely filled f shell, e.g.,  $Yb^{2+} (4f^{14})$

In addition (+II) and (+IV) states exist for elements that are close to these states. Thus  $\text{Sm}^{2+}$  and  $\text{Tm}^{2+}$  occur with  $4f^6$  and  $4f^{13}$  arrangements and  $\text{Pr}^{4+}$  and  $\text{Nd}^{4+}$  have  $4f^1$  and  $4f^2$  arrangements. The (+III) state is always the most common and the most stable. The only (+IV) and (+II) states which have any aqueous chemistry are  $\text{Ce}^{4+}$ ,  $\text{Sm}^{2+}$  and  $\text{Yb}^{2+}$ .

The lanthanide elements resemble each other much more closely than do a horizontal row of the transition elements. This is because the lanthanides effectively have only one stable oxidation state, (+III). Thus in this series it is possible to compare the effects of small changes in size and nuclear charge on the chemistry of these elements.

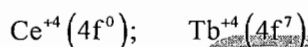
The +2 ions are readily oxidised and the +4 ions are readily reduced to the +3 ion (most stable oxidation state).

**+2 oxidation state:**



In liquid  $\text{NH}_3$  both are soluble.

**+4 oxidation state:**



+2 and +4 oxidation states are less stable than +3.



Less stable

More stable

Therefore salts of  $\text{M}^{+2}$  ions lanthanides act as strong reducing agent.  
(Self oxidise and they reduced another)



Salts of  $\text{M}^{+4}$  ion lanthanide ions acts as strong oxidising agent

Eu and Yb behaves as similar to alkaline earth behaves as similar to alkaline earth metal (largest size).

♦ That is why ceric ammonium nitrate,  $[\text{Ce}^{(+IV)}(\text{NO}_3)_6]^{2+}$  act as an oxidising agent or oxidant in redox titration.

**Soln.**

$\text{Ce}^{(+IV)}$  is stable in aq. system.

C.N. of  $\text{Ce}^{(IV)} = 12$

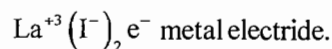
Structure  $\Rightarrow$  Icosahedral

Nitrate is acting as a bidentate ligand. (Monoanionic)

♦  $\text{LaI}_2$  &  $\text{CeI}_2$

Oxidation state of La and Ce in these complexes +3 oxidation state.

When in any compound electron behaves as anion then such compound are called electrides.



- Due to this free electron  $\text{LaI}_2$  acts as electricity conduct and has metallic property (Insulator).
- Lanthanide element are very reactive and liberate hydrogen gas with boiling water and reactivity same as alkaline metal.

**Abundance and number of Isotopes:**

Elements with an even atomic number (i.e. an even number of protons in the nucleus) are more abundant than their neighbours with odd atomic numbers (Harkin's Rule).

- Elements with even atomic number also have more stable isotopes.
- Elements with odd atomic number never have more than two stable isotopes.



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aqueous

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Throughout the periodic table the stability of a nucleus is related to both the number of neutrons and the number of protons in the nucleus.

#### Naturally occurring isotopes:

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
4	1	7	0	7	2	7	1	7	1	6	1	7	2

• Number of stable nuclei with odd and even number of neutrons and odd and even atomic numbers.

Atomic Number	Number of Neutrons	Stable Nuclei
Even	Even	164
Even	Odd	55
Odd	Even	50
Odd	Odd	4

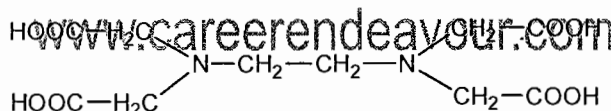
#### Separation of the Lanthanide Elements:

The properties of metal ions are determined by their size and charge. The lanthanides are all typically trivalent and are almost identical in size, and so their chemical properties are almost identical. The separation of one lanthanide from another is an exceedingly difficult task, almost as difficult as the separation of isotopes of one element.

#### Some of the separation methods are discussed below:

**Precipitation:** With a limited amount of precipitating agent the substance with the lowest solubility is precipitated most rapidly and most completely. Suppose hydroxyl ions are added to a solution containing a mixture of  $Ln(NO_3)_3$ . The weakest base  $Lu(OH)_3$  is precipitated first, and the strongest base  $La(OH)_3$  is precipitated last. The precipitate contains more of the elements at the right of the series. Thus the solution contains more of the elements at the left of the series. The precipitate can be filtered off. Only partial separation is effected, but the precipitate can be redissolved in  $HNO_3$  and the process repeated to obtain greater purity.

**Complex Formation:** A mixture of lanthanide ions is treated with a complexing agent such as EDTA (ethylenediaminetetraacetic acid). All the ions form complexes. Those ions at the right hand side of the lanthanide series such as  $Lu^{3+}$  form the strongest complexes as they have the smallest ions. Oxalates of the lanthanides are insoluble. However, addition of oxalate ions to this solution does not give a precipitate since the  $Ln^{3+}$  ions are all complexed with EDTA.



EDTA

If some acid is added to the solution, the least stable EDTA complexes are dissociated. This releases ions at the left hand side of the series  $Ce^{3+}$ ,  $Pr^{3+}$ ,  $Nd^{3+}$  which are immediately precipitated as the oxalates. These are filtered off. Separation is not complete, so the oxalates are redissolved and the process repeated many times.

#### Solvent Extraction:

The heavier  $Ln^{3+}$  ions are more soluble in tri-n-butylphosphate than are the lighter  $Ln^{3+}$  ions. Their solubilities in water and ionic solvents, however, are reversed. The ratios of the partition coefficients of  $La(NO_3)_3$  and  $Gd(NO_3)_3$  between a solution of the metal ions in strong  $HNO_3$  and tri-n-butylphosphate is 1 : 1.06. This difference is quite small, but by using a continuous counter-current apparatus a very large number of partitions can be performed automatically.

### Valency Change:

A few lanthanides have oxidation states of (+IV) or (+II). The properties of  $\text{Ln}^{4+}$  or  $\text{Ln}^{2+}$  are so different from those of  $\text{Ln}^{3+}$  that separation is fairly easy.

Cerium can be separated from lanthanide mixtures quite easily as it is the only lanthanide which has  $\text{Ln}^{4+}$  ions stable in aqueous solution. Oxidizing a solution containing a mixture of  $\text{Ln}^{3+}$  ions with  $\text{NaOCl}$  under alkaline conditions produces  $\text{Ce}^{4+}$ . Because of the higher charge,  $\text{Ce}^{4+}$  is much smaller and less basic than  $\text{Ce}^{3+}$  or any other  $\text{Ln}^{3+}$ . The  $\text{Ce}^{4+}$  is separated by carefully controlled precipitation of  $\text{CeO}_2$  or  $\text{Ce}(\text{IO}_3)_4$ , leaving the trivalent ions in solution.

Alternatively  $\text{Ce}^{4+}$  can readily be extracted from other  $\text{Ln}^{3+}$  lanthanides by solvent extraction in  $\text{HNO}_3$  solution using tributyl phosphate. Ninety-nine per cent pure Ce can be obtained in one stage from a mixture containing 40% Ce.

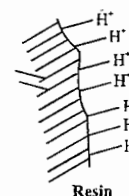
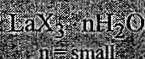
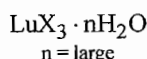
In a similar way the properties of  $\text{Eu}^{2+}$  are very different from those of  $\text{Ln}^{3+}$ . Europium sulphate  $\text{Eu}^{2+} \text{SO}_4^{2-}$  resembles the Group 2 sulphates and is insoluble in water.  $\text{Ln}^{3+}$  sulphates are soluble. If a solution of  $\text{Ln}^{3+}$  ions is reduced electrolytically using a mercury cathode, or by using zinc amalgam, then  $\text{Eu}^{2+}$  will be produced. If  $\text{H}_2\text{SO}_4$  is present  $\text{EuSO}_4$  will be precipitated. This can be filtered off. ( $\text{Sm}^{2+}$  and  $\text{Yb}^{2+}$  may also be produced in the same way, but these are oxidized slowly by water.)

Valency change is still a useful method for purifying Ce and Eu despite the advent in recent years of ion exchange.

**Ion Exchange:** This is the most important, the most rapid and most effective general method for the separation and purification of the lanthanides. A solution of lanthanide ions is run down a column of synthetic ion-exchange resin such as Dowex-50. This is a sulphonated polystyrene and contains the functional groups— $\text{SO}_3\text{H}$ . The  $\text{Ln}^{3+}$  ions are absorbed onto the resin and replace the hydrogen atom on— $\text{SO}_3\text{H}$ .



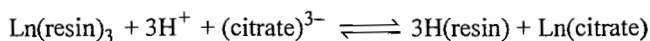
The individual salts are hydrated to varying degrees. Lutetium, being smallest, is most heavily hydrated, while lanthanum, being largest, is least hydrated.



This means that the hydrated radius of lanthanum is smallest, while that of lutetium is the largest. The hydrated mixture is passed down a chromatographic column containing a synthetic ion exchange resin.

The binding of lanthanide cations to the anionic sites of the exchange resin involves electrostatic attractions. Hence smaller the hydrated radius of the ion, more strongly it is bound. The lanthanum hydrated ion, being smallest, becomes attached to the resin immediately, that is, it becomes absorbed at the top of the column. The lutetium hydrated ion, being the largest, becomes absorbed at the bottom of the column.

The  $\text{H}^+$  ions produced are washed through the column. Then the metal ions are eluted, that is are washed off the column in a selective manner. The eluting agent is a complexing agent, for example a buffered solution of citric acid/ ammonium citrate, or a dilute solution of  $(\text{NH}_4)_3(\text{H}_2\text{EDTA})$  at pH 8. Consider the citrate case. An equilibrium is set up:



As the citrate solution flows down the column,  $\text{Ln}^{3+}$  ions are removed from the resin and form the citrate complex. A little lower down the column the  $\text{Ln}^{3+}$  ions go back onto the resin. As the citrate solution runs down the column, the metal ions form complexes alternately with the resin and the citrate solution many times. The metal ion gradually travels down the column, and eventually passes out of the bottom of the column as the citrate complex. The smaller lanthanide ions such as  $\text{Lu}^{3+}$  form stronger complexes with the citrate ions than do the larger ions like  $\text{La}^{3+}$ . Thus the smaller and heavier ions spend more time in solution, and less time on the column,





and are thus eluted from the column first. The different metal ions present separate into bands which pass down the column. The progress of the bands may be followed spectroscopically by atomic fluorescence. The solution leaving the column is collected by means of an automatic fraction collector in separate containers. By this means the individual elements can be separated. The metals may be precipitated as insoluble oxalates, and then heated to give the oxides.

By using a long ion-exchange column the elements may be obtained 99.9% pure with one pass.

#### Chemical Properties of (+III) Compounds:

The metals are all soft and silvery white. They are electropositive and therefore they are very reactive. The heavier metals are less reactive than the lighter ones because they form a layer of oxide on the surface. The chemical properties of the group are essentially the properties of trivalent ionic compounds.

**The sum of the first three ionization energies varies with minima at  $\text{La}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Lu}^{3+}$  which are associated with attaining an empty, half full or full  $f$  shell. Maxima occur at  $\text{Eu}^{3+}$  and  $\text{Yb}^{3+}$  associated with breaking a half full or full shell.**

The standard reduction potentials  $E^0$  are all high. They vary in a regular way over a small range from  $-2.48$  to  $-2.26$  volts, depending on the size of the ions.

The lanthanides are all much more reactive than Al ( $E^0 = -1.66$  volts) and are slightly more reactive than Mg ( $E^0 = -2.37$  volts). Thus they react slowly with cold water, but more rapidly on heating.

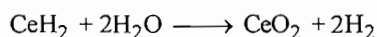


The hydroxides  $\text{Ln}(\text{OH})_3$  are precipitated as gelatinous precipitates by the addition of  $\text{NH}_4\text{OH}$  to aqueous solutions. These hydroxides are ionic and basic. They are less basic than  $\text{Ca}(\text{OH})_2$  but more basic than  $\text{Al}(\text{OH})_3$  which is amphoteric. The metals, oxides and hydroxides all dissolve in dilute acids, forming salts.  $\text{Ln}(\text{OH})_3$  are sufficiently basic to absorb  $\text{CO}_2$  from the air and form carbonates. The basicity decreases as the ionic radius decreases from Ce to Lu. Thus  $\text{Ce}(\text{OH})_3$  is the most basic, and  $\text{Lu}(\text{OH})_3$  which is the least basic, is intermediate between scandium and yttrium in basic strength. The decrease in basic properties is illustrated by the hydroxides of the later elements dissolving in hot concentrated  $\text{NaOH}$ , forming complex



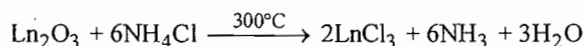
The metals tarnish readily in air, and on heating in  $\text{O}_2$  they all give oxides  $\text{Ln}_2\text{O}_3$ . Yb and Lu form a protective oxide film, which prevents the bulk of the metal forming the oxide unless it is heated to  $1000^\circ\text{C}$ . The one exception is Ce which forms  $\text{Ce}_2\text{O}_3$  rather than  $\text{Ce}_2\text{O}_3$ . The oxides are ionic and basic. **Basic strength decreases as the ions get smaller.**

The metals react with  $\text{H}_2$ , but often require heating up to  $300\text{--}400^\circ\text{C}$  to start the reaction. The products are solids of formula  $\text{LnH}_2$ . Eu and Yb both have a tendency to form divalent compounds and  $\text{EuH}_2$  and  $\text{YbH}_2$  are salt-like hydrides and contain  $\text{M}^{2+}$  and two  $\text{H}^-$ . The other all form hydrides  $\text{LnH}_2$  which are black, metallic and conduct electricity. These are better formulated as  $\text{Ln}^{3+}$ ,  $2\text{H}^-$  and an electron which occupies a conduction band. **In addition Yb forms a nonstoichiometric compound approximating to  $\text{YbH}_{2.5}$ .** The hydrides are remarkably stable to heat, often up to  $900^\circ\text{C}$ . They are decomposed by water, and react with oxygen.

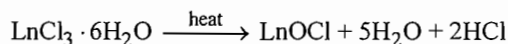


These 'dihydrides' take up H if heated under pressure, and all except Eu form salt-like hydrides  $\text{LnH}_3$  made up of  $\text{Ln}^{3+}$  and three  $\text{H}^-$ . These do not have a delocalized electron, and do not show metallic conduction.

The anhydrous halides  $\text{MX}_3$  can be made by heating the metal and halogen, or by heating the oxide with the appropriate ammonium halide.



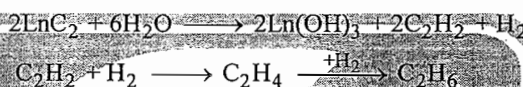
The fluorides are very insoluble, and can be precipitated from solutions of  $\text{Ln}^{3+}$  by addition of  $\text{Na}^+\text{F}^-$  or  $\text{HF}$ . This is used as a test for the lanthanides in qualitative analysis. However, with excess  $\text{F}^-$ , the smaller lanthanide ions may form soluble complexes  $[\text{LnF}(\text{H}_2\text{O})_n]^{2+}$ . The chlorides are deliquescent and soluble, and crystallize with six or seven molecules of water of crystallization. If the hydrated halides are heated, they form oxohalides instead of dehydrating to anhydrous halides.



Heating  $\text{CeX}_3 \cdot (\text{H}_2\text{O})_n$  results in  $\text{CeO}_2$ . The bromides and iodides are similar to the chlorides.

At elevated temperatures, the lanthanides react with B, giving  $\text{LnB}_4$  and  $\text{LnB}_6$ .

On arc-melting the metals with C in an inert atmosphere they form carbides of stoichiometry  $\text{LnC}_2$  and  $\text{Ln}_4(\text{C}_2)_3$ . The carbides can also be made by reducing  $\text{Ln}_2\text{O}_3$  with C in an electric furnace.  $\text{LnC}_2$  are more reactive than  $\text{CaC}_2$ . They react with water, giving ethyne and also some hydrogen,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ . They also show metallic conductivity. They do not contain  $\text{Ln}(\text{+II})$  and are best described as acetylides of  $\text{Ln}^{3+}$  and  $\text{C}_2^{2-}$  -with the extra electron in a conduction band.

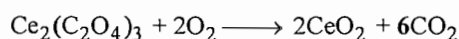
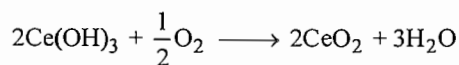


At elevated temperatures the metals also react with N, P, As, Sb and Bi, giving  $\text{LnN}$  etc. The latter is hydrolysed by water in a similar way to  $\text{AlN}$ :



#### Oxidation State (+IV):

The only (+IV) lanthanide which exists in solution and has any aqueous chemistry is  $\text{Ce}^{4+}$ . It is rare to find 4+ ions in solution. The high charge on the ion leads to it being heavily hydrated, and except in strongly acidic solutions the hydrated  $\text{Ce}^{4+}$  is hydrolysed, giving polymeric species and  $\text{H}^+$ .  $\text{Ce}(\text{+IV})$  solutions are widely used as an oxidizing agent in volumetric analysis instead of  $\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ . In classical analysis burettes containing  $\text{Ce}^{4+}$  must be washed with acid, since washing with water gives the hydrated ion. Aqueous cerium(IV) solutions can be prepared by oxidizing a  $\text{Ce}^{3+}$  solution with a very strong oxidizing agent such as ammonium peroxodisulphate  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .  $\text{Ce}(\text{+IV})$  is also used in organic reactions, for example the oxidation of alcohols, aldehydes and ketones at the  $\alpha$ -carbon atom. The common compounds are  $\text{CeO}_2$  (white when pure) and  $\text{CeO}_2 \cdot (\text{H}_2\text{O})_n$  (a yellow gelatinous precipitate).  $\text{CeO}_2$  can be obtained by heating the metal, or  $\text{Ce}(\text{OH})_3$  or  $\text{Ce}_2^{III}(\text{oxalate})_3$ , in air.  $\text{CeO}_2$  has a fluorite type of structure. It is insoluble in acids and alkalis, but dissolves if reduced, giving  $\text{Ce}^{3+}$  solutions.



$\text{Ce}(\text{SO}_4)_2$  (formerly called cerie sulphate) is well known and is yellow like  $\text{K}_2\text{CrO}_4$ .  $\text{CeF}_4$  is obtained from  $\text{CeF}_3$  and  $\text{F}_2$ . It is white, and is rapidly hydrolysed by water. It has a three-dimensional crystal structure with the metal at the centre of a square antiprism. A number of complexes are stable, for example ammonium cerium(IV) nitrate  $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ . The crystal structure is unusual and contains bidentate  $\text{NO}_3^-$  groups. The Ce atom has a coordination number of 12, and the shape is an **icosahedron**. Two of the ions may be replaced by phosphine ligands  $\text{Ph}_3\text{PO}$ , giving a neutral 10-coordinate complex  $[\text{Ce}^{\text{IV}}(\text{NO}_3)_4(\text{Ph}_3\text{PO})_2]$ . The elements Pr, Nd, Tb and Dy also form (+IV) states. These are generally unstable, occur only as solids, and are found as fluorides or oxides which may be nonstoichiometric.

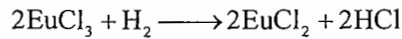


or HF.  
hanide  
tallize  
alides

### Oxidation State (+II):

The only (+II) states which have any aqueous chemistry are  $\text{Sm}^{2+}$ ,  $\text{Eu}^{2+}$  and  $\text{Yb}^{2+}$ .

**The most stable divalent lanthanide is  $\text{Eu}^{2+}$ .** This is stable in water, but the solution is strongly reducing.  $\text{Eu}^{II}\text{SO}_4$  can be prepared by electrolysis of solutions, when the divalent sulphate is precipitated.  $\text{Eu}^{III}\text{Cl}_2$  can be made as a solid by reducing  $\text{Eu}^{III}\text{Cl}_3$  with  $\text{H}_2$ .



Aqueous  $\text{Eu}^{3+}$  solutions can be reduced by Mg, Zn, zinc amalgam or electrolytically to give  $\text{Eu}^{2+}$ .  $\text{EuH}_2$  is ionic and similar to  $\text{CaH}_2$ .  $\text{Eu(II)}$  resembles Ca in several ways:

1. The insolubility of the sulphate and carbonate in water.
2. The insolubility of the dichloride in strong HCl.
3. The solubility of the metals in liquid  $\text{NH}_3$ .

One major difference between Eu and Ca is that the dihalides  $\text{EuX}_2$  have a magnetic moment of 7.9 Bohr magnetons corresponding to seven unpaired electrons, whereas Ca compounds are diamagnetic.

The couple  $\text{Eu}^{3+}|\text{Eu}^{2+}$  has a standard reduction potential of  $-0.41$  volts. This is about the same as for  $\text{Cr}^{3+}|\text{Cr}^{2+}$ , and these are both about the strongest reducing agents that do not reduce water.

$\text{Yb}^{2+}$  and  $\text{Sm}^{2+}$  can be prepared by electrolytic reduction of their trivalent ions; in aqueous solution. However, the  $\text{Ln}^{2+}$  ions are readily oxidized by air. These two elements form hydroxides, carbonates, halides, sulphates and phosphates.

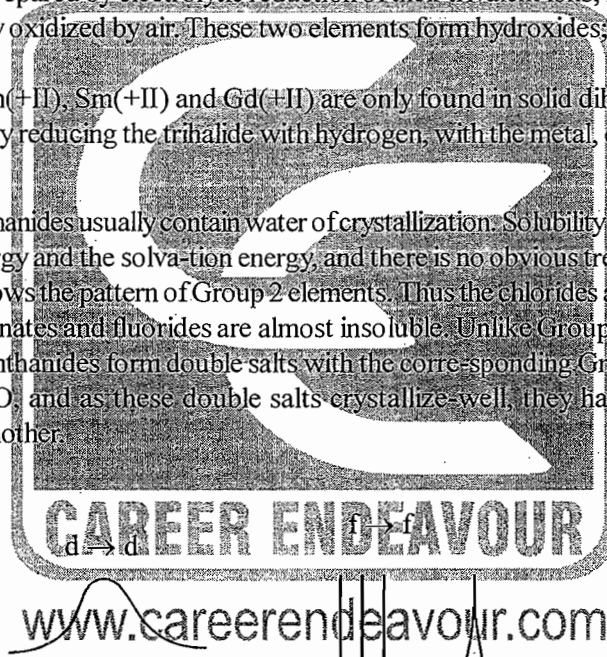
The states  $\text{Nd(II)}$ ,  $\text{Pm(II)}$ ,  $\text{Sm(II)}$  and  $\text{Gd(II)}$  are only found in solid dihalides  $\text{LnCl}_2$  and  $\text{LnI}_2$ . These dihalides can be made by reducing the trihalide with hydrogen, with the metal, or with sodium amalgam.

### Solubility:

Salts of the lanthanides usually contain water of crystallization. Solubility depends on the small difference between the lattice energy and the solvation energy, and there is no obvious trend in the group. The solubility of many of the salts follows the pattern of Group 2 elements. Thus the chlorides and nitrates are soluble in water and the oxalates, carbonates and fluorides are almost insoluble. Unlike Group 2, however, the sulphates are soluble. Many of the lanthanides form double salts with the corresponding Group 1 or ammonium salts, e.g.  $\text{Na}_2\text{SO}_4 \cdot \text{Ln}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , and as these double salts crystallize well, they have been used to separate the lanthanides from one another.

### Colour and Spectra:

Many trivalent lanthanide ions are strongly coloured both in the solid state and in aqueous solution. The colour seems to depend on the number of unpaired  $f$  electrons. Elements with  $(n)f$  electrons often have a similar colour to those with  $(14-n)f$  electrons. However, the elements in other valency states do not all have colours similar to their isoelectronic  $3+$  counterparts.



Broad peak

Line like and sharp peak

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**Main smith colour sequence:** $f^0, f^7, f^{14}$  are colourless

Lu <sup>3+</sup>	f <sup>0</sup>	colourless	Lu <sup>3+</sup>	f <sup>14</sup>	colourless
Ce <sup>3+</sup>	f <sup>1</sup>	colourless	Yb <sup>3+</sup>	f <sup>13</sup>	colourless
Pr <sup>3+</sup>	f <sup>2</sup>	green	Tm <sup>3+</sup>	f <sup>12</sup>	palegreen
Nd <sup>3+</sup>	f <sup>3</sup>	lilac	Er <sup>3+</sup>	f <sup>11</sup>	rose – pink
Pm <sup>3+</sup>	f <sup>4</sup>	pink	Ho <sup>3+</sup>	f <sup>10</sup>	pale yellow
Sm <sup>3+</sup>	f <sup>5</sup>	yellow	Dy <sup>3+</sup>	f <sup>9</sup>	yellow
Eu <sup>3+</sup>	f <sup>6</sup>	palepink	Tb <sup>3+</sup>	f <sup>8</sup>	pale pink
Gd <sup>3+</sup>	f <sup>7</sup>	colourless	Gd <sup>3+</sup>	f <sup>7</sup>	colourless

**Ce<sup>3+</sup> and Tb<sup>3+</sup> transition 4f → 5d.**

$$\Delta l = 1$$

Stronger absorption than forbidden f-f transitions. The electronic configuration of Ce<sup>3+</sup> of f<sup>1</sup> and Yb<sup>3+</sup> is f<sup>13</sup>, loss of one electron gives the extra stability of an empty or half full shell.

Ce<sup>4+</sup> = Ligand → Metal charge transfer

Sm<sup>2+</sup> = Metal → Ligand charge transfer

Tb<sup>3+</sup> = f → d transition

Eu and Yb are non conductor because they don't form electric.

**Colour of (Lanthanide) Ln<sup>3+</sup>, Ln<sup>2+</sup> and their isoelectronic Ln<sup>3+</sup>:**

Ce <sup>4+</sup>	Orange-red	4f <sup>0</sup>	La <sup>3+</sup>	Colourless
Sm <sup>2+</sup>	Blood red	4f <sup>6</sup>	Eu <sup>3+</sup>	Pale Pink
Eu <sup>2+</sup>	Pale greenish yellow	4f <sup>7</sup>	Gd <sup>3+</sup>	Colourless
Yb <sup>2+</sup>	Yellow	4f <sup>14</sup>	Lu <sup>3+</sup>	Colourless

Colour arises because light of a particular wavelength is absorbed in the visible region. The wavelength absorbed corresponds to the energy required to promote an electron to a higher energy level. In the lanthanides spin orbit coupling is more important than crystal field splitting. In the spectra of transition metals, crystal field splitting is of major importance. All but one of the lanthanide ions show absorptions in the visible or near-UV regions of the spectrum. The exception is Lu<sup>3+</sup> which has a full f shell. These colours arise from f-f transitions. Strictly these transitions are Laporte forbidden (since the change in the subsidiary quantum number is zero). Thus the colours are pale because they depend on relaxation of the rule. The f orbitals are deep inside the atom. Thus they are largely shielded from environmental factors such as the nature and number of ligands which form of the complexes, and from vibration of the ligands. Thus the position of the absorption band (i.e., the colour) does not change with different ligands. Vibration of the ligands changes the external fields. However, this only splits the various spectroscopic states by about 100 cm<sup>-1</sup>, so the absorption bands are unusually sharp. The lanthanides are used for wavelength calibration of instruments because of their sharp absorption bands. For an f electron the subsidiary quantum number  $l = 3$ , so  $m_l$  may have values 3, 2, 1, 0, -1, -2, -3. Thus a large number of transitions are usually possible. This is in marked contrast to the transition elements where d-d spectra give absorption bands whose position changes from ligand to ligand, and the width of the peak is greatly broadened because of the vibration of the ligands. It is also possible to get transitions from the 4f to the 5d level. Such transitions give broader peaks and their position is affected by the nature of the ligands.



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Absorption spectra of lanthanide ions are useful both for the qualitative detection and the quantitative estimation of lanthanides. Lanthanide elements are sometimes used as biological tracers for drugs in humans and animals. This is because lanthanide elements can quite easily be followed in the body by spectroscopy, because their peaks are narrow and very characteristic.

$Ce^{3+}$  and  $Yb^{3+}$  are colourless because they do not absorb in the visible region. However, they show exceptionally strong absorption in the UV region, because of transitions from  $4f$  to  $5d$ . Absorption is very strong for two reasons. Since  $\Delta l = 1$  this is an allowed transition and so give stronger absorption than forbidden  $f-f$  transitions. Furthermore, promotion of electrons in these ions is easier than for other ions. The electronic configuration of  $Ce^{3+}$  is  $f^1$  and  $Yb^{3+}$  is  $f^{14}$ . Loss of one electron gives the extra stability of an empty or half full shell.  $f-d$  peaks are broad, in contrast to the narrow  $f-f$  peaks.

Charge transfer spectra are possible due to the transfer of an electron from the ligand to the metal. This is more probable if the metal is in a high oxidation state or the ligand has reducing properties. Charge transfer usually produces intense colours. The orange-red yellow colour of  $Ce^{4+}$  solutions arises from charge transfer rather than  $f-f$  spectra. The blood red colour of  $Sm^{2+}$  is also due to charge transfer.

### Magnetic Properties:

$La^{3+}$  and  $Ce^{4+}$  have  $f^0$  configuration, and  $Lu^{3+}$  has an  $f^{14}$  configuration. These have no unpaired electrons, and are diamagnetic. All other  $f$  states contain unpaired electrons, and are therefore paramagnetic.

The magnetic moment of transition elements may be calculated from the equation:

$$\mu_{(S+L)} = \sqrt{4S(S+1) + L(L+1)}$$

$\mu_{(S+L)}$  is the magnetic moment in Bohr magnetons calculated using both the spin and orbital momentum contributions.  $S$  is the resultant spin quantum number and  $L$  is the resultant orbital momentum quantum number. For the first row transition elements, the orbital contribution is usually quenched out by interaction with the electric field of the ligands in its environment. Thus as a first approximation the magnetic moment can be calculated. Using the simple spin only formula, ( $\mu_s$  is the spin only magnetic moment in Bohr magnetons,  $S$  is the resultant spin quantum number and  $n$  is the number of unpaired electrons.)

$$\mu_s = \sqrt{4S(S+1)}$$

$$\mu_s = \sqrt{n(n+2)}$$

This simple relationship works with  $La^{3+}$  ( $f^0$ ), and two of the lanthanides  $Gd^{3+}$  ( $f^7$ ) and  $Lu^{3+}$  ( $f^{14}$ ).

$La^{3+}$  and  $Lu^{3+}$  have no unpaired electrons,  $n = 0$  and  $\mu_s = \sqrt{0(0+2)} = 0$   
 $Gd^{3+}$  has seven unpaired electrons,  $n = 7$  and

$$\mu_s = \sqrt{7(7+2)} = \sqrt{63} = 7.9 \text{ BM}$$

The other lanthanide ions do not obey this simple relationship. The  $4f$  electrons are well shielded from external fields by the overlying  $5s$  and  $5p$  electrons. Thus the magnetic effect of the motion of the electron in its orbital is not quenched out. Thus the magnetic moments must be calculated taking into account both the magnetic moment from the unpaired electron spins and that from the orbital motion. This also happens with the second and third row transition elements. However, the magnetic properties of the lanthanides are fundamentally different from those of the transition elements. In the lanthanides the spin contribution  $S$  and orbital contribution  $L$  couple together to give a new quantum number  $J$ .

$J = L - S$  when the shell is less than half full  
 and  $J = L + S$  when the shell is more than half full

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The magnetic moment  $m$  is calculated in Bohr magnetons (BM) by:

$$\mu = g\sqrt{J(J+1)}$$

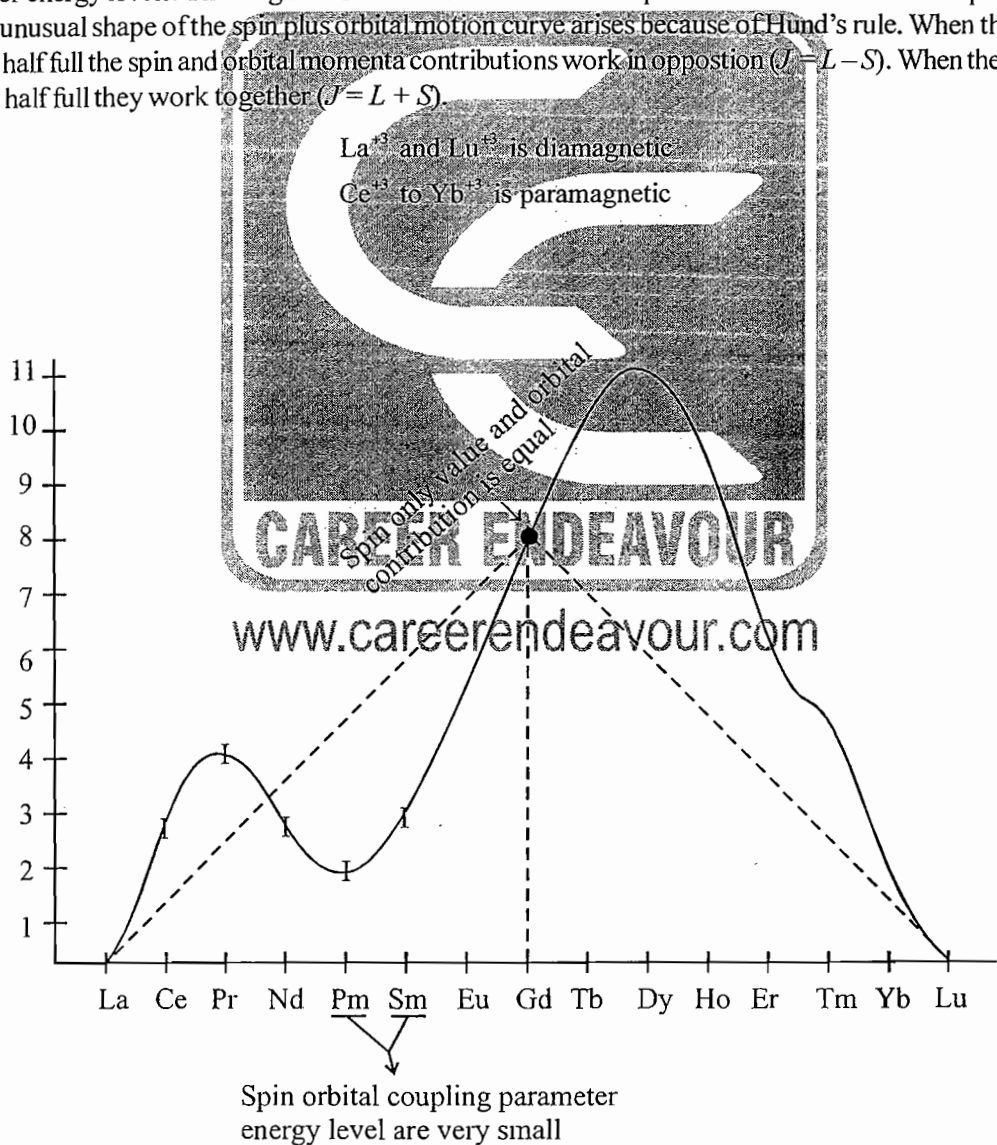
where

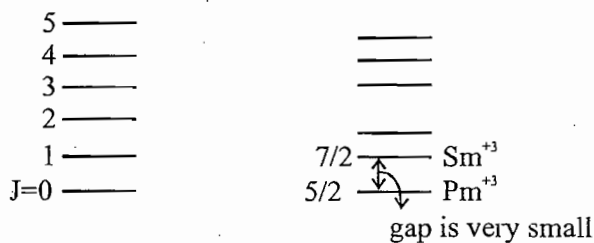
$$g = 1 + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Following figure shows the calculated magnetic moments for the lanthanides using both the simple spin only formula, and the coupled spin plus orbital momentum formula. For most of the elements there is excellent agreement between the calculated values using the coupled spin + orbital momentum formula and experimental values measured at 300 K. The range of experimental values are shown as bars.

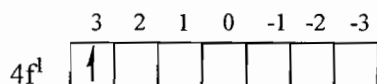
The agreement for  $\text{Eu}^{3+}$  is poor, and that for  $\text{Sm}^{3+}$  is not very good. The reason is that with  $\text{Eu}^{3+}$  the spin orbit coupling constant is only about  $300 \text{ cm}^{-1}$ . This means that the difference in energy between the ground state and the next state is small. Thus the energy of thermal motion is sufficient to promote some electrons and partially populate the higher state. Because of this the magnetic properties are not solely determined by the ground state configuration. Measuring the magnetic moment at a low temperature prevents the population of higher energy levels. The magnetic moment of  $\text{Eu}^{3+}$  at low temperature is close to zero as expected.

The unusual shape of the spin plus orbital motion curve arises because of Hund's rule. When the  $f$  level is less than half full the spin and orbital momenta contributions work in opposition ( $J = L - S$ ). When the  $f$  shell is more than half full they work together ( $J = L + S$ ).





$Ce^{+3}$



$$\ell = 3, s = 1/2$$

$$2s + 1 = 2$$

Ground state term of  $Ce^{+3} = {}^2F_{7/2}$

$$J = L - S = 3 - \frac{1}{2} = \frac{5}{2}$$

Ground state term:

Magnetic property:

$$\mu = g\sqrt{J(J+1)} \text{ B.M.}$$

$g$  = Lande's splitting factor.

or

gyromagnetic ratio

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

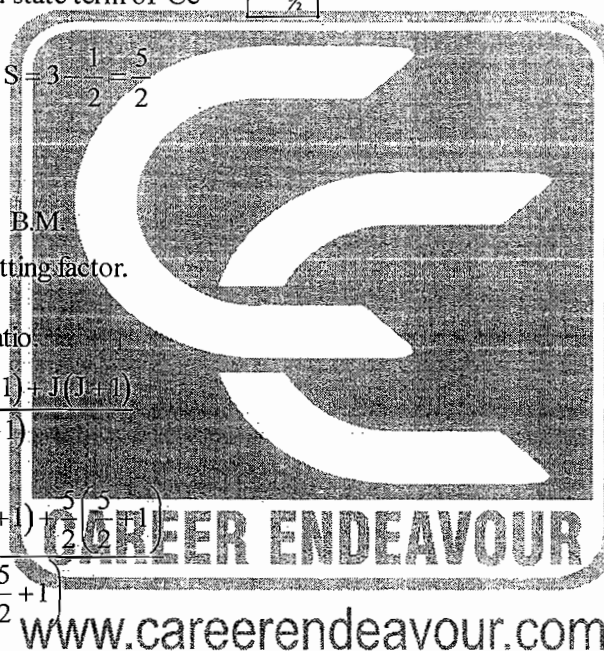
$$g = 1 + \frac{\frac{1}{2}\left(\frac{1}{2}+1\right) - 3(3+1) - \frac{5}{2}\left(\frac{5}{2}+1\right)}{2 \times \frac{5}{2}\left(\frac{5}{2}+1\right)}$$

$$g = \frac{70 - 10}{70} = \frac{60}{70} = \frac{6}{7}$$

$$\mu = g\sqrt{J(J+1)} = \frac{6}{7}\sqrt{\frac{35}{7}}; \frac{6}{7} \times \frac{5.9}{2}; \mu = \frac{17.7}{7} = 2.53$$

$$\mu = 2.53 \text{ B.M.} \quad \text{calculated}$$

$$\mu = 2.3 \text{ to } 2.5 \quad \text{observed}$$



Ln	M <sup>3+</sup>	Config. Ground State <sub>term</sub>	No. of unpaired e <sup>-</sup>	Colour	Magnetic Moment [B.M.]	
					calculated	observed
La	4f <sup>0</sup>	<sup>1</sup> S <sub>0</sub>	0	colourless	0	0
Ce	4f <sup>1</sup>	<sup>2</sup> F <sub>5/2</sub>	1	colourless	2.54	2.3 - 2.5
Pr	4f <sup>2</sup>	<sup>3</sup> H <sub>4</sub>	2	green	3.58	3.4 - 3.6
Nd	4f <sup>3</sup>	<sup>4</sup> I <sub>9/2</sub>	3	lilac	3.62	3.5 - 3.6
Pm	4f <sup>4</sup>	<sup>5</sup> L <sub>4</sub>	4	pink	2.68	-
Sm	4f <sup>5</sup>	<sup>6</sup> H <sub>5/2</sub>	5	yellow	0.85	1.4 - 1.7
Eu	4f <sup>6</sup>	<sup>7</sup> F <sub>0</sub>	6	pale pink	0	3.3 - 3.5
Gd	4f <sup>7</sup>	<sup>8</sup> S <sub>7/2</sub>	7	colourless	7.94	7.9 - 8.0
Tb	4f <sup>8</sup>	<sup>7</sup> F <sub>6</sub>	6	pale pink	9.72	9.5 - 9.8
Dy	4f <sup>9</sup>	<sup>6</sup> H <sub>15/2</sub>	5	yellow	10.65	10.4 - 10.6
Ho	4f <sup>10</sup>	<sup>5</sup> I <sub>8</sub>	4	yellow	10.6	10.4 - 10.7
Er	4f <sup>11</sup>	<sup>4</sup> I <sub>15/2</sub>	3	rose-pink	9.58	9.4 - 9.6
Tm	4f <sup>12</sup>	<sup>3</sup> H <sub>6</sub>	2	pale green	7.56	7.1 - 7.6
Yb	4f <sup>13</sup>	<sup>2</sup> F <sub>7/2</sub>	1	colourless	4.54	4.3 - 4.9
Lu	4f <sup>14</sup>	<sup>1</sup> S <sub>0</sub>	0	colourless	0	0

### Lanthanide contraction:

In general trend ionic radii in main group increases on moving down because extra shells of electron are added.

$$\text{Li}^+ = 0.76\text{\AA}, \quad \text{Na}^+ = 1.02\text{\AA}, \quad \text{K}^+ = 1.38\text{\AA}$$

While on going left to right ionic radii across any period decreases.

This 'p' is partly due to increase in number of charges on nucleus and also increase in charge of ions.

$$\text{Na}^+ = 1.02\text{\AA}, \quad \text{Mg}^{2+} = 0.720\text{\AA}, \quad \text{Al}^{3+} = 0.533\text{\AA}$$

The d and f orbitals do not shield the nuclear charge effectively. Thus there is slight reduction in size of ions just after 10d or 14f electron have been filled. The latter is called lanthanide contraction.

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### Covalent Radii:

Sc	$\frac{0.12}{1.44}$	Ti	$\frac{0.10}{1.32}$	V	$\frac{0.5}{1.22}$	Cr	1.17	Mn	1.17	Fe	1.17
Y	1.62	Zr	1.45	Nb	1.34	Mo	1.34	Tc		Ru	1.24
La	1.69	Hf	1.44	Ta	1.34	W	1.30	Re	1.28	Os	1.26

→ 14 Lanthanide elements

The steady decrease in ionic radius all along the series amounting in all to 0.22Å is called lanthanide contraction.



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### Lanthanide Contraction:

Covalent and ionic radii normally increase on descending a group in the periodic table due to the presence of extra filled shells of electrons. On moving from left to right across a period, the covalent and ionic radii decrease. This is because the extra orbital electrons incompletely shield the extra nuclear charge. Thus all the electrons are pulled in closer. The shielding effect of electrons decreases in the order  $s > p > d > f$ . The contraction in size from one element to another is fairly small. However, the additive effect over the 14 lanthanide elements from Ce to Lu is about  $0.2 \text{ \AA}$ , and this is known as the lanthanide contraction.

The progressive (steady) decrease in the radii of the atoms and ions of the lanthanides with increasing atomic number is called lanthanide contraction. Thus lanthanum has the largest radius while lutetium has the smallest.

**Reason :** The shielding of one  $f$  electron by another from the effects of the nuclear charge is quite weak because of the diffused (larger) shapes of the  $f$ -orbitals (i.e.,  $f$ -orbitals have poor shielding effect). Hence with increasing atomic number and nuclear charge, the effective nuclear charge,  $Z_{\text{eff}}$  experienced by  $4f$ -electron increases from left to right. This increase in  $Z_{\text{eff}}$  causes a shrinkage in the radii of atoms or ions on moving from La to Lu. This accumulation of successive shrinkage is called lanthanide contraction.

### Consequences of Lanthanide Contraction:

1. The hardness, melting point and boiling points of the elements all increase from Ce to Lu. This is because the attraction between the atoms in metallic lattice increases as the size decreases.
2. The properties of an ion depend on its size and its charge. The  $\text{Ln}^{3+}$  lanthanide ions change by only a small amount from one element to the next, and their charge is the same, and so their chemical properties are very similar.
3. Since  $\text{Lu}^{3+}$  is the smallest ion it is the most heavily hydrated, while  $\text{La}^{3+}$  being large is least hydrated.
4. Though the lanthanides do not form complexes very extensively, since  $\text{Lu}^{3+}$  is the smallest ion the complexes formed by  $\text{Lu}^{3+}$  are the stronger.
5.  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  are the largest ions so  $\text{La}(\text{OH})_3$  and  $\text{Ce}(\text{OH})_3$  are the strongest bases, while  $\text{Lu}(\text{OH})_3$  is least basic.
6. The lanthanide contraction reduces the radii of the last four elements in the series below that for Y in the preceding transition series. Since the size of the heavier lanthanide ions, particularly  $\text{Dy}^{3+}$  and  $\text{Ho}^{3+}$ , are similar to that of  $\text{Y}^{3+}$  it follows that their chemical properties are also very similar. As a result the separation of these elements is very difficult.
7. Because of this contraction in size across the lanthanide series, the elements which follow in the third transition series are considerably smaller than would otherwise be expected. The normal size increase  $\text{Sc} \rightarrow \text{Y} \rightarrow \text{La}$  disappears after the lanthanides. Thus pairs of elements such as Zr/Hf, Nb/Ta and Mo/W are almost identical in size. The close similarity of properties in such a pair makes chemical separation very difficult. The sizes of the third row of transition elements are very similar to those of the second row of transition elements. Thus the second and third rows of transition elements resemble each other more closely than do the first and second rows.

### Complexes:

The lanthanide ions  $\text{Ln}^{3+}$  have a high charge, which favours the formation of complexes. However, the ions are rather large ( $1.03\text{--}0.86 \text{ \AA}$ ) compared with the transition elements ( $\text{Cr}^{3+} = 0.615 \text{ \AA}$ ,  $\text{Fe}^{3+} = 0.55 \text{ \AA}$  (low spin)) and consequently they do not form complexes very readily. Complexes with amines are not formed in aqueous solution because water is a stronger ligand than the amine. However amine-complexes can be made in non-aqueous solvents. Very-few stable complexes are formed with CO,  $\text{CN}^-$  and organometallic groups. This is in contrast to the transition metals. The difference arises because the  $4f$  orbitals are well shielded and are buried beneath  $5s$  and  $5p$  orbitals. Thus they cannot take part in  $\pi$  back bonding, whereas in the transition elements the  $d$  orbitals are involved in  $\pi$  bonding. The most common and stable complexes are those with chelating oxygen ligands such as citric acid, oxalic acid,  $\text{EDTA}^{4-}$  and acetylacetonate. These complexes frequently have high and variable coordination numbers, and water or solvent molecules are often attached to the central metal.  $\beta$ -Diketone complexes of  $\text{Eu}^{3+}$  and  $\text{Pr}^{3+}$  dissolved in organic solvents are used as lanthanide shift reagents in nmr spectroscopy.



Coordination numbers below 6 are uncommon, and occur only with bulky ligands such as (2,6-dimethylphenyl) and  $[\text{N}(\text{SiMe}_3)_2]^-$ . In contrast to the transition elements, the coordination number 6 is not common. The most common coordination numbers are 7, 8 and 9 and these give a variety of stereochemistries. The relatively large size of the lanthanide ions makes possible the coordination of greater number of ligands (less strain). Coordination numbers 10 and 12 occur with the larger (lighter) lanthanides and small chelating ligands  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ .

Complexes with monodentate oxygen ligands are much less stable than the chelates, and tend to dissociate in aqueous solution. There are hardly any complexes with nitrogen donor ligands except ethylenediamine and  $\text{NCS}^-$ , and these are decomposed by water. Fluoride complexes  $\text{LnF}_{(\text{aq})}^{2+}$  are formed particularly by the smaller ions, but chloride complexes are not formed in aqueous media or concentrated HCl. This is an important distinction between the lanthanide and actinide groups.

$\text{Ce}^{4+}$  is smaller and more highly charged, and  $[\text{Ce}(\text{NO}_3)_6]^{2-}$  is formed in the non-aqueous solvent  $\text{N}_2\text{O}_4$ , and is 12-coordinate. Each uses two oxygen atoms to coordinate to the metal.

The lanthanides form no complexes with p bonding ligands, and the lack of p bonding is attributed to the unavailability of the *f* orbitals for bonding.

It is difficult to explain the bonding in complexes with high coordination numbers. If one *s* orbital, three *p* orbitals and all six *d* orbitals in the valency shell are used for bonding, this accounts for a maximum coordination number of 9. The higher coordination number of 10 and 12 present a problem. They imply either participation of *f* orbitals in bonding, or bond orders of less than one.

#### Co-ordination Number

Co-ordination Number	Complex	Shape
4	$[\text{Lu}(\text{2,6-dimethylphenyl})_4]^-$	Tetrahedral
6	$[\text{Ce}^{\text{IV}}\text{Cl}_6]^{2-}$	Octahedral
6	$[\text{Er}(\text{NCS})_6]^{3-}$	Octahedral.
7	$[\text{Y}(\text{acetylacetonate})_3(\text{H}_2\text{O})]^-$	Monocapped trigonal prism.
8	$[\text{La}(\text{acetylacetonate})_3(\text{H}_2\text{O})_2]^-$	Square antiprism
8	$[\text{Ce}^{\text{IV}}(\text{acetylacetonate})_4]^{2-}$	Square antiprism.
8	$[\text{Eu}(\text{acetylacetonate})_3(\text{phenanthroline})]^-$	Square antiprism
8	$[\text{Ho}(\text{tropalionate})_4]^-$	Dodecahedral.
9	$[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$	Tricapped trigonal prism.
10	$[\text{Ce}^{\text{IV}}(\text{NO}_3)_4(\text{Ph}_3\text{PO})_2]^{2-}$	Complex
12	$[\text{Ce}^{\text{IV}}(\text{NO}_3)_6]^{2-}$	Icosahedral. [Each $\text{NO}_3^-$ is bidentate]



**The application of Lanthanide metals and their compounds:**

**Misch Metal:** 50% Ce, 40% La, 7% Fe, 3% others metals. This is added to steel to improve its strength and workability. Small amount of misch metal is also used as lighter flints.

**Pyrophoric Alloys:** 40% Ce, 44% La + Nd, 5% Fe and rest is Al, Ca, C and Si. It is used in the preparation of ignition devices such as tracer bullets and shells.

2.  $\text{La}_2\text{O}_3$  is used in Crooke's lenses, which gives protection from UV light by absorbing it.

3.  $\text{CeO}_2$  is used in polish glass.

4. Gas mantles are treated with a mixture of 1%  $\text{CeO}_2$  and 99%  $\text{ThO}_2$  to increase the amount of light emitted by coal gas flames.

5. Lanthanide oxides are also used as phosphorus in colour TV tubes.

6. Lanthanide elements are present in warm super-conductors such as  $\text{La}_{(2-x)}\text{Ba}_x\text{CuO}_{(4-y)}$  and  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and others.

7. 3-diketone complexes of  $\text{Eu}^{3+}$  and  $\text{Pr}^{3+}$  dissolved in organic solvents are used as Lanthanide shift reagents in NMR spectroscopy.

**Shift Reagents:**

The shift reagents are ions in the rare earth (lanthanide series) coordinated to organic ligands, generally  $\beta$ -diketone complexes of  $\text{Eu}^{3+}$  and  $\text{Pr}^{3+}$ . More recent shift reagents are  $\text{Eu}(\text{dpm})_3$  and  $\text{Eu}(\text{fod})_3$ . Their name came from tris-(dipivalomethanato) europium and tris-1, 1, 1, 2, 2, 3, 3-heptafluoro-7, 7-dimethyl-1, 5-octanedionatoeuropium.

Shift reagents provide a method for spreading out NMR absorption patterns without increasing the strength of the applied magnetic field. Addition of shift reagents to appropriately functionalized samples results in substantial magnifications of the chemical shift differences of non-equivalent protons. There are two major applications of the shift reagent to structure determination.

(i) To simplify the spectrum.

(ii) To assign the protons from the data on the response curve.

Effectiveness of the shift reagent analysis may be increased by the use of low temperature NMR.



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## THE ACTINIDES

The 14 elements from atomic number 90 thorium to atomic number 103 lawrencium are called the actinide elements. However, the electronic structures of the actinides do not follow the simple pattern found in the lanthanides.

Immediately after La the 4*f* orbitals become appreciably lower in energy than the 5*d* orbitals. Thus in the lanthanides the electrons fill the 4*f* orbitals in a regular way (apart from minor differences where it is possible to attain a half filled shell). It might have been expected that after Ac the 5*f* orbitals would become lower in energy than the 6*d* orbitals. However, for the first four actinide elements Th, Pa, U and Np the difference in energy between 5*f* and 6*d* orbitals is small. Thus in these elements (and their ions) electrons may occupy the 5*f* or the 6*d* levels, or sometimes both. Later in the actinide series the 5*f* orbitals do become appreciably lower in energy. Thus from Pu onwards the 5*f* shell fills in a regular way, and the elements become very similar.

**Table :** The elements, their electronic configuration and their oxidation states:

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

### OXIDATION STATES:

The (+II) state is quite rare. Am<sup>2+</sup> has an *f*<sup>7</sup> configuration. It is the analogue of Eu<sup>2+</sup> in the lanthanides, but it only exists in the solid as the fluoride. In contrast Cf<sup>2+</sup>, Es<sup>2+</sup>, Fm<sup>2+</sup> and No<sup>2+</sup> exist as ions in solution. Their properties are like the Group 2 metals, particularly Ba<sup>2+</sup>. It is the most stable oxidation state for No, and corresponds to an *f*<sup>14</sup> arrangement.

The actinides all have an oxidation state of (+III), like the lanthanides. However, this is not always the most stable oxidation state in the actinides. (+III) is not the most stable oxidation state for the first four elements Th, Pa, U and Np. For example, U<sup>3+</sup> is readily oxidized in air, and in solution. The (+III) state is the most stable state for the later elements 95Am @ 103Lw (excluding 102No). Their properties are similar to those of the lanthanides.

The most stable oxidation states for the first four elements are Th (+IV), Pa (+V) and U (+VI). These high oxidation states involve using all the outer electrons (including *f* electrons) for bonding. Though Np (+VII) exists, it is oxidizing and the most stable state is (+V). Pu shows all the oxidation states from (+III) to (+VII), but the most stable is Pu(IV). Am has a range of oxidation states from (+II) to (+VI). However, for Am and almost all the remaining elements the (+III) state is the most stable.

The (+IV) state exists for all the elements from <sub>90</sub>Th to <sub>97</sub>Bk, and it is the most important state for Th and Pu. M<sup>4+</sup> ions are known in acid solution, and are precipitated by F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and IO<sub>3</sub><sup>-</sup> ions. The elements all form solid dioxides MO<sub>2</sub> and fluorides MF<sub>4</sub>.

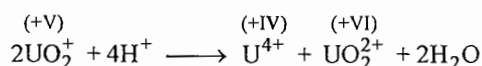


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The (+V) state occurs for the elements  ${}_{91}\text{Pa} \rightarrow {}_{95}\text{Am}$ , and it is the most stable state for Pa and Np. A few solid compounds are known.  $\text{M}^{5+}$  ions do not occur in solution, but  $\text{MO}_2^+$  ions exist between pH 2–4, and these oxoions are linear  $[\text{O}—\text{M}—\text{O}]^+$ . These ions disproportionate rapidly in solution, but are found in solid compounds.



The (+VI) state exists as fluorides  $\text{MF}_6$  for the elements U, Np, Pu and Am. The (+VI) state is more widely found as the dioxo ion  $\text{MO}_2^{2+}$ . This ion is linear  $[\text{O}—\text{M}—\text{O}]^{2+}$ , and is stable. It exists both in solution and in crystals. The crystal structure of uranyl nitrate  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  consists of the linear  $(\text{O}—\text{U}—\text{O})^{2+}$  ion surrounded by two  $\text{NO}_3^-$  groups and two  $\text{H}_2\text{O}$  molecules. The groups are bidentate, so two O atoms from each bond to the U. O atoms from the two  $\text{H}_2\text{O}$  atoms also bond to U, giving a coordination number of 8. Similarly in the crystal structure of sodium uranyl acetate  $\text{Na}[\text{UO}_2(\text{CH}_3\text{COO})_3]$  the acetate groups are bidentate using both O atoms, so U is eight-coordinate.

The lower oxidation states tend to be ionic, and the higher ones covalent.

### Complexes:

The  $5f$  orbitals can spatially extend outside the  $6s$  and  $6p$  orbitals to a much greater degree than  $4f$  orbitals can extend outside  $5s$  and  $5p$  orbitals. As a result, the valence orbitals of actinides can interact more strongly with the ligands than the valence orbitals of lanthanides. For this reason the actinides are more prone to form complexes than are the lanthanides. Halide and oxoanionic ligands, like oxalate, sulfate and phosphate form complexes with actinides very readily. Even  $\pi$ -bonding ligands, such as phosphines and thioethers can form complexes with actinides. Since the energies of  $5f$ ,  $6d$  and  $7s$  shells are very close to each other, hybridization is possible between these orbitals. Thus actinide complexes are known in a range of stereochemistries. Examples include, octahedral, tetrachlorobis (triethylphosphine) uranium(IV),  $[\text{UCl}_4\{\text{P}(\text{C}_2\text{H}_5)_3\}_2]$  and dodecahedral, tetraoxalatothorate(IV) ion,  $[\text{Th}(\text{C}_2\text{O}_4)_4]^{4-}$ .

**Actinide Contraction:** There is a steady and consistent decrease of the ionic radii of actinides with increasing atomic number. The phenomenon is analogous to lanthanide contraction and, therefore, is referred to as actinide contraction. The decrease in size is attributed to the imperfect shielding of one  $5f$  electron by another in the same shell. While traversing the actinide series, the nuclear charge and the valence electrons both increases by one unit at each step, due to diffused shape of  $5f$ -orbitals the electrons do not shield the nuclear charge efficiently. The valence electrons are strongly pulled towards the nucleus and the size decreases.

**OCCURENCE AND PREPARATION OF THE ELEMENTS:** All the elements after  ${}^{82}\text{Pb}$ , that is from  ${}^{83}\text{Bi}$  onwards, have unstable nuclei and undergo radioactive decay. The elements up to and including  ${}^{92}\text{U}$  occur in nature and have been known for a long time. Th and U occur at all on the earth is because the isotopes  ${}^{232}_{90}\text{Th}$ ,  ${}^{235}_{92}\text{U}$  and  ${}^{238}_{92}\text{U}$  have half lives sufficiently long for some to have remained since the earth was formed

( $t_{1/2}$  for  ${}^{238}_{92}\text{U}$  is  $4.5 \times 10^9$  years, and for is  $7.04 \times 10^8$  years).

The radioactivity produces self-heating. Ten grams of  ${}^{239}\text{Pu}$  generates 0.02 watts of heat. This cannot be used as a large scale power source since this isotope is fissile and thus undergoes nuclear fission. (The critical mass of  ${}^{239}\text{Pu}$  is only about 1 kg.)

Up to 10% Th is found in Monazite sand, mixed with the lanthanides as  $(\text{ThLn})\text{PO}_4$ . It is also found as the ore thorite  $\text{ThSiO}_4$ . U is mined as the ore pitchblende  $\text{UO}_2$ . Very small amounts of Ac, Pa, Np and Pu have been detected in these ores. These four elements are only available by synthetic routes. Plutonium is formed in large amounts by irradiating uranium fuel in nuclear reactors. This is important because plutonium is fissile, and can be used for military purposes (to make atomic weapons) and also as a fuel for nuclear generating stations to make electricity.



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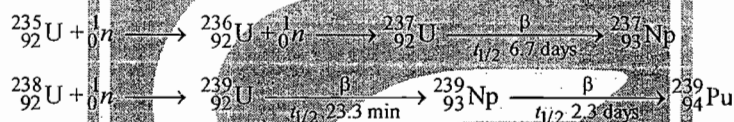
The elements with higher atomic numbers than U are called the transuranium elements. These have all been produced artificially in the period since 1940. These elements were produced using a nuclear reactor to irradiate suitable elements with neutrons. They are also made using an accelerator to bombard a sample with particles (He nuclei), or the nuclei of light atoms such as C, B, N, O or Ne. Most of the transuranium elements were discovered (first made) at the University of California.

**Preparation of the Actinides**

The early members of the series are usually formed by (n, g) reactions which are usually followed by b emission.

The U -fuel rod is irradiated with *slow neutrons* (of energy 1 MeV). A neutron may be captured by the nucleus in a (n, g) reaction. The neutron increases the mass number of the nucleus by one, and some energy is released as g radiation. Further neutrons may be added in a similar way. Addition of neutrons increases the neutron to proton ratio (the n/p ratio). This eventually makes the nucleus unstable because it contains too many neutrons. The nuclei decay by converting a neutron into a proton and a b particle (electron). This reduces the n/p ratio and also increases the atomic number by one. Thus a new element is formed, one place to the right in the periodic table of the original element.

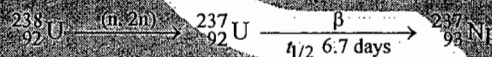
When the fuel rod is eventually removed from the reactor, it is processed, and the new elements can be recovered. There is not much use for Np so normally only Pu is recovered. (Pu is useful both as a nuclear fuel, and for weapons.)



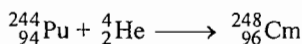
The yield of the heavier elements is controlled by two factors:

1. The half lives of the various isotopes.
2. By their ability to absorb neutrons, that is their neutron cross-section.

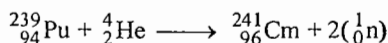
Isotopes of elements after Pu can be made by a succession of (n, g) reactions starting with Pu in a nuclear reactor.



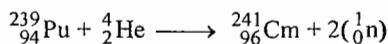
The stepwise addition of slow neutrons is tedious. A quicker method is to subject the sample to a very high flux or density of fast neutrons, without allowing time for the intermediate products to decay. This happened during the hydrogen bomb explosions when elements  ${}_{99}\text{Es}$  einsteinium and  ${}_{100}\text{Fm}$  fermium were formed. As yet this does not, provide a convenient and practicable synthetic route! In reactor fuel elements  ${}^{238}\text{U}$  adds a fast neutron and then loses two neutrons.



An alternative method is to bombard the sample with small ions. These must have sufficient energy to overcome the coulombic repulsion between the ion and the heavy nucleus. These ions are given a high kinetic energy of motion by accelerating them to a great speed in a linear accelerator, or in a cyclotron. The simplest ion used is the a particle (that is a He nucleus). These increase the mass number by four and the atomic number by two.

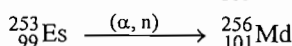
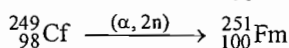
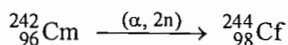
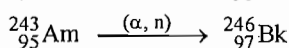
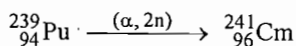


Often the addition of the helium nucleus upsets the ratio of neutrons to protons, and one or more neutrons are emitted. The equations for nuclear reactions may either be written showing all the particles in the equation, e.g.,

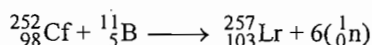
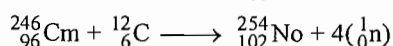
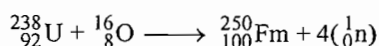
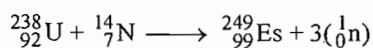


or in a shorthand way with the particles added and lost shown in brackets:





The heaviest elements were obtained by bombarding the sample with accelerated ion  $\text{B}^{5+}$ ,  $\text{C}^{6+}$ ,  $\text{N}^{7+}$  or  $\text{O}^{8+}$ .



### General Properties

The elements are all silvery metals. Their melting points are moderately high, but are considerably lower than those for the transition elements. The size of the ions decreases regularly along the series, because the extra charge on the nucleus is poorly screened by the  $f$  electrons. This results in an 'actinide contraction' similar to the lanthanide contraction. Comparison of the  $M^{3+}$  ionic radii with those for lanthanides shows that the actinide and lanthanide ions are very similar in size. Hence their chemical properties are alike. However, the actinides have much higher densities and a much greater tendency to form complexes.

The actinides are reactive metals like lanthanum and the lanthanides. They react with hot water, and tarnish in air, forming an oxide coating. In the case of Th this coating is protective, but this is not so with the others. The metals react readily with HCl, but reaction with other acids is slower than expected. Concentrated  $\text{HNO}_3$  passivates Th, U and Pu. The metals are basic and do not react with NaOH.

### Thorium:

Thorium is by no means rare. It comprises 8.1 ppm of the earth's crust and is the thirty-ninth most abundant element. The main source is monazite sand in which it occurs up to 10% as the phosphate, mixed with phosphates of the lanthanides. Thorium is also found as uranothorite (a mixed silicate of Th and U). Monazite is treated with NaOH. The insoluble hydroxides are filtered off and dissolved in HCl. The pH is adjusted to 6, when the hydroxides of Th(IV), U(IV) and Ce(IV) are precipitated. This separates them from the trivalent lanthanides. The hydroxide precipitates are dissolved in 6M HCl and extracted with tri-butylphosphate and kerosene. If required the metal can be obtained by reducing  $\text{ThO}_2$  with Ca, or  $\text{ThCl}_4$  with Ca or Mg.

The only stable oxidation state is Th(+IV), and the  $\text{Th}^{4+}$  ion is known both in the solid and in solution.  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  is the best known salt, and it is very soluble in water. In dilute solutions hydrated ions  $(\text{Th}(\text{H}_2\text{O})_n)^{4+}$  exist, and on adding NaOH, a precipitate of  $\text{Th}(\text{OH})_4$  is produced. The oxide  $\text{ThO}_2$  is formed by heating the nitrate, or by heating the metal in air. The oxide is white and has the highest melting point of any oxide ( $3220^\circ\text{C}$ ). Anhydrous halides  $\text{ThX}_4$  are formed by direct reaction. They are also formed by strongly heating the oxide with the appropriate halogen acid or heating the oxide with  $\text{CCl}_4$  at  $600^\circ\text{C}$ . The halides are high melting and white. On strong heating  $\text{ThI}_4$  decomposes to the elements. This has been used to purify the metal by the van Arkel method. The halides hydrolyse in moist air, giving oxohalides  $\text{ThOX}_2$ . The white colour of Th(IV) compounds is associated with the absence of  $d$  or  $f$  electrons. The high charge of  $\text{Th}^{4+}$  favours the formation of complexes.

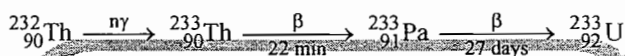


## Some high coordination number:

Complex	Coordination Number	Shape
• $K_4[Th(oxalate)_4] \cdot 4H_2O$	8	Square antiprism
• $(NH_4)_4[ThF_8]$	9	Tricapped trigonal prism $[ThF_9]$ Sharing to edges to give infinite chains.
• $Mg[Th(NO_3)_6]$	12	Icosahedral the $NO_3^-$ group are bidentate.

The two industrial uses of Th are as follows:

1. When thorium dioxide containing 1% cerium is heated in a gas flame it emits a brilliant white light. Because of this it was widely used for making incandescent gas mantles. At one time gas lighting provided the main source of artificial light. (Electric light bulbs and fluorescent tubes have largely replaced gas lighting except for mobile use, e.g. in caravans. However, making gas mantles still accounts for half the Th produced.)
2. Naturally occurring thorium is almost entirely  $^{232}Th$ . This isotope is not fissionable, but if irradiated in the outer part of a nuclear reactor,  $^{235}U$  is formed.



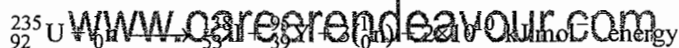
This isotope of uranium does not occur in nature, and has a half life of  $1.6 \times 10^5$  years. It is fissionable.

**URANIUM:** Uranium ores were originally mined as a source of Ra, which was used for radiotherapy treatment of cancer. Small amounts of U were (and still are) used to produce pale yellow or green coloured glass. This glass fluoresces under UV light. Some uranium oxide is used for colouring ceramics.

Uranium vanadates such as carnotite  $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$  constitute the chief ore of U. It occurs as a distinctive yellow or green-yellow crust, or in sandstones and soft aggregates. U is also mined as oxide ores, the most important being uraninite and pitchblende. These are black-brown coloured, nonstoichiometric and approximate to  $UO_2$ .

The stoichiometric oxides  $UO$ ,  $U_2O_3$  and  $UO_3$  are black-brown, green-black and orange-yellow respectively. U is the forty-eighth most abundant element in the earth's crust.

**Nuclear Fission:** Naturally occurring uranium contains three isotopes: 99.3%  $^{238}U$ , 0.7%  $^{235}U$  and traces of  $^{234}U$ . The isotope  $^{235}U$  is fissile, and if it is irradiated with thermal (slow) neutrons the nucleus breaks up into two smaller nuclei. At least a million times more energy is liberated by this fission than from a chemical reaction. The nucleus may split giving several products one such reaction being:



If one of the neutrons evolved splits another  $^{235}U$  nucleus then a self-perpetuating nuclear chain reaction will be started. This liberates energy at a constant rate. Since three neutrons are evolved per fission, these could in principle split three further  $^{235}U$  nuclei. This would liberate even more neutrons and start a branched chain reaction. This would run out of control, liberating energy at an ever increasing rate, resulting in an explosion.

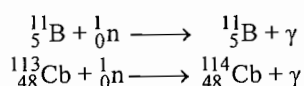
It is very difficult to start and maintain a chain reaction. The neutrons produced by the fission are 'fast neutrons', and have energies of  $2 \times 10^8$  kJ mol<sup>-1</sup>. They tend to escape and are not very effective at causing further fission. They are much less effective than 'slow neutrons' with an energy of about 2 kJ mol<sup>-1</sup>. (These are sometimes called 'thermal neutrons', because their energy is equivalent to thermal energy attainable at room temperature.)



Two things can be done to increase the chance of a chain reaction.

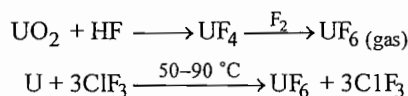
1. The fast neutrons may be slowed down by collision with atoms of hydrogen, deuterium or carbon. These materials are called moderators.
2. A large enough mass of  ${}^{235}_{92}\text{U}$  is needed to ensure that sufficient neutrons hit another fissile U nucleus rather than escape. Thus there is a critical mass. The size of this depends on the shape of the material and on its purity. A sphere has the minimum surface area, which minimizes the chance of neutrons escaping. Rods or sheets have a much larger area: hence neutrons can escape more easily. The chance of neutrons causing fission increases if the proportion of the fissile isotope is increased. Thus it is usual to 'enrich' the fuel.

Control rods are used to make sure that the reaction does not get out of control. The control rods absorb neutrons. The rods are lowered into the reactor to absorb neutrons and slow it down, or are raised out of the reactor to allow it to speed up. Control rods may be made of boron steel, cadmium or hafnium.



To get an explosion, conditions must be such that the neutron propagation factor is greater than one. This means that more than one neutron from each fission is effective at causing another fission. This is called a branched chain reaction. To attain these conditions bomb grade fuel is very highly enriched. It may contain up to 80%  ${}^{235}\text{U}$ . Normally the energy liberated melts the radioactive material, thus allowing it to spread out. Because of the increased surface area, more neutrons escape: hence the chain reaction ceases. Only if the fissile material is prevented from spreading out by some form of containment will a chain reaction result in an explosion. The temperatures reached are similar to that of the sun, and there is no casing that will withstand such temperatures. The first atomic bomb dropped on Hiroshima used  ${}^{235}\text{U}$ . Two sub-critical masses of enriched  ${}^{235}\text{U}$  at opposite ends of a gun barrel were shot together by a small conventional explosion, which held them together long enough for a nuclear explosion to occur. In a nuclear reactor, the neutron propagation factor is very close to one. This means that only one neutron from each fission is allowed to cause another fission. Thus the release of energy is controlled, and can be used for peaceful purposes such as generating electricity. The surplus neutrons may escape, or may be absorbed by the neutron absorbing control rods or by  ${}^{238}\text{U}$  which is also present in the fuel rods.

Fuel is usually enriched to between 2% and 4% of  ${}^{235}\text{U}$  for civil nuclear reactors in power stations. A much higher enrichment is required for bombs and reactors for submarines (70% or 80%)! There are four methods of separating the isotopes of U: thermal diffusion, gaseous diffusion, electromagnetic separation and using a gas centrifuge. Large scale separation is now carried out using the different rates of diffusion of gaseous  ${}^{235}\text{UF}_6$  and  ${}^{238}\text{UF}_6$  the gas centrifuge method is increasing in importance.



When  ${}^{238}\text{U}$  absorbs neutrons it forms the heavier element Pu which is itself fissile and can be used as a nuclear fuel. Since a larger quantity of Pu may be formed than the quantity of  ${}^{235}\text{U}$  that is consumed, the reactor is called a fast breeder reactor.

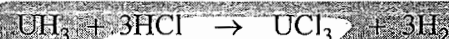
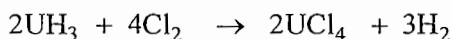
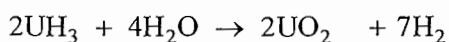


**Chemical properties**

Uranium and the next three elements Np, Pu and Am show oxidation states of (+III), (+IV), (+V) and (+VI). These are similar to each other, except that the most stable state drops from U(VI) to Np(V) to Pu(IV) to Am(III). In the (+III) and (+IV) states the compounds are similar to lanthanides. The ions formed in the oxidation states (+III), (+IV), (+V) and (+VI) are  $M^{3+}$ ,  $M^{4+}$ ,  $MO_2^+$  and  $MO_2^{2+}$  respectively. Oxidation-reduction reactions are rapid between  $M^{3+}$  and  $M^{4+}$ , or and as these only involve the transfer of an electron. Oxidation of  $M^{4+}$  to is slow because it involves transfer of oxygen.

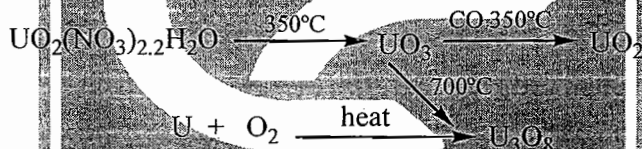
**Hydrides**

Uranium reacts with hydrogen even at room temperature, though the reaction is faster at 250°C, giving  $UH_3$  as a black pyrophoric powder. The hydride is very reactive, and is often more suitable than the metal for making other compounds.



**Oxides**

$UO_2$  is brown-black and occurs in pitchblende.  $U_3O_8$  is greenish black, whilst  $UO_3$  is orange-yellow. Some reactions are given:



All three oxides are basic and dissolve in acids.  $UO_3$  dissolves in  $HNO_3$  forming the yellow uranyl ion  $[O=U=O]^{2+}$ . Crystallizing this solution gives uranyl nitrate  $UO_2(NO_3)_2 \cdot (H_2O)_x$ . The number of molecules of water of crystallization may be two, three or six depending on whether it is crystallized from fuming, concentrated or dilute  $HNO_3$ . Crystals of the dihydrate have an unusual eight-coordinate structure. This comprises a linear  $[O=U=O]^{2+}$  group perpendicular to a hexagon of six oxygen atoms, four from two bidentate  $NO_3^-$  groups and two from water molecules.

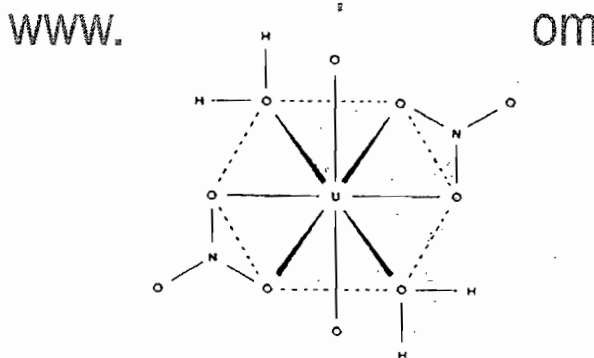


Fig: Uranyl nitrate dihydrate  $UO_2(NO_3)_2 \cdot 2H_2O$







### Further Extension of The Periodic Table

The actinide series is complete at element 103, lawrencium. Elements 104–109 have been reported recently and are *d*-block elements

The IUPAC proposed a system for naming elements with  $Z > 100$

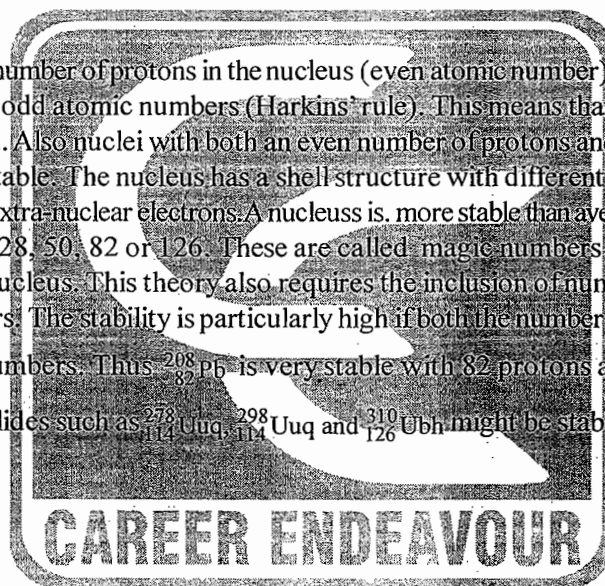
1. The names are derived by using roots, for the three digits in the atomic number of the element and adding the ending-ium. The roots for the numbers are

0	1	2	3	4	5	6	7	8	9
nil	un	bi	tri	quad	pent	hex	sep	oct	enn

2. In certain cases the names, are shortened; for example, biium and triium are shortened to bium and trium, and enn nil is shortened to ennil.
3. The symbol for the element is made up from the first letters from the roots which make up the name. The strange mixture of Latin and Greek roots has been chosen to ensure that the symbols are all different. Though the names are written as a complete word. In the examples below a hyphen has been inserted between each part of the name to make them more understandable. These hyphens should be omitted.

### Magic Numbers

Elements with an even number of protons in the nucleus (even atomic number) are usually more stable than their neighbours, with odd atomic numbers (Harkins' rule). This means that they are less likely to decay, and are more abundant. Also nuclei with both an even number of protons and an even number of neutrons are more likely to be stable. The nucleus has a shell structure with different energy levels broadly similar to the energy levels of extra-nuclear electrons. A nucleus is more stable than average if the number of neutrons or protons is 2, 8, 20, 28, 50, 82 or 126. These are called magic numbers and can be explained by the shell structure of the nucleus. This theory also requires the inclusion of numbers 114, 164 and 184 in the series of magic numbers. The stability is particularly high if both the number of protons and the number of neutrons are magic numbers. Thus  ${}_{82}^{208}\text{Pb}$  is very stable with 82 protons and  $208 - 82 = 126$  neutrons. This suggests that nuclides such as  ${}_{114}^{278}\text{Uuq}$ ,  ${}_{114}^{298}\text{Uuq}$  and  ${}_{126}^{310}\text{Ubn}$  might be stable enough to exist.



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South Delhi : 28-A/11, Jia Sarai, Near-IIT Hauz Khas, New Delhi-16, Ph : 011-26851008, 26861009

North Delhi : 33-35, Mall Road, G.T.B. Nagar (Opp. Metro Gate No. 3), Delhi-09, Ph: 011-65462244, 65662255