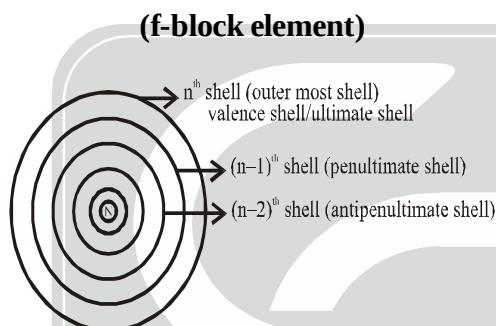


Inner Transition Elements

Lanthanide and Actinide :



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.

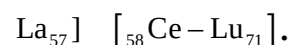
In past they were called rare earth metals.

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

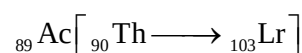
General configuration:

$$(n-2)f^{1 \text{ to } 14} (n-1)d^{1 \text{ or } 0} ns^2$$

Lanthanum is not element of lanthanide series.



Only Pm (Promathium) is radioactive element.



${}_{90}\text{Th}$ ${}_{90}\text{Pd}$ ${}_{92}\text{U}$ [${}_{93}\text{NP} \rightarrow$ onward]



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.

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 $\text{Ce}^{3+} f^1, \text{Pr}^{3+} f^2, \text{Nd}^{3+} f^3, \dots \text{Lu}^{3+} f^{14}$.

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 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.

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

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:

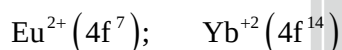
1. A noble gas configuration, e.g., $\text{Ce}^{4+} (4f^0)$
2. A half filled f shell, e.g., Eu^{2+} and $\text{Tb}^{4+} (4f^7)$
3. A completely filled f shell, e.g., $\text{Yb}^{2+} (4f^{14})$

In addition (+II) and (+IV) states exist for elements that are close to these states. Thus Sm^{2+} and Tm^{2+} occur with $4f^6$ and $4f^{13}$ arrangements and Pr^{4+} and 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 Ce^{4+} , Sm^{2+} and 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.

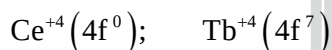
The +2 ions are readily oxidised and the +4 ions are readily reduced to the +3 ion (most stable oxidation state).

+2 oxidation state:

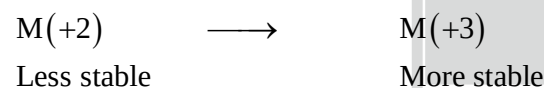


In liquid NH_3 both are soluble.

+4 oxidation state:

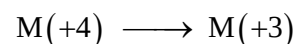


+2 and +4 oxidation states are less stable than +3.



Therefore salts of M^{+2} ions lanthanides act as strong reducing agent.

(Self oxidise and they reduced another)



Salts of 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 $[\text{Ce}^{(+IV)} (\text{NO}_3)_6]$ 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)

♦ **LaI_2 & 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 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.

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

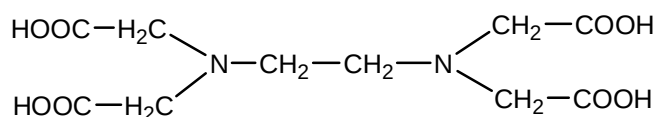
Separation of the Lanthanide Elements:

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 $\text{Ln}(\text{NO}_3)_3$. The weakest base $\text{Lu}(\text{OH})_3$ is precipitated first, and the strongest base $\text{La}(\text{OH})_3$ 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 $\text{La}(\text{NO}_3)_3$ and $\text{Gd}(\text{NO}_3)_3$ 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 Ln^{4+} or Ln^{2+} are so different from those of Ln^{3+} that separation is fairly easy.

Cerium can be separated from lanthanide mixtures quite easily as it is the only lanthanide which has Ln^{4+} ions stable in aqueous solution. Oxidizing a solution containing a mixture of Ln^{3+} ions with NaOCl under alkaline conditions produces Ce^{4+} . Because of the higher charge, Ce^{4+} is much smaller and less basic than Ce^{3+} or any other Ln^{3+} . The Ce^{4+} is separated by carefully controlled precipitation of CeO_2 or $\text{Ce}(\text{IO}_3)_4$, leaving the trivalent ions in solution.

Alternatively Ce^{4+} can readily be extracted from other Ln^{3+} lanthanides by solvent extraction in HNO_3 solution using tributyl phosphate. Ninety-nine per cent pure Ce can be obtained in one stage from a mixture containing 40% Ce.

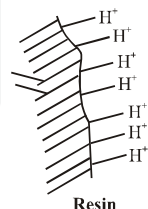
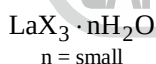
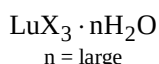
In a similar way the properties of Eu^{2+} are very different from those of Ln^{3+} . Europium sulphate $\text{Eu}^{2+} \text{SO}_4^{2-}$ resembles the Group 2 sulphates and is insoluble in water. Ln^{3+} sulphates are soluble. If a solution of Ln^{3+} ions is reduced electrolytically using a mercury cathode, or by using zinc amalgam, then Eu^{2+} will be produced. If H_2SO_4 is present EuSO_4 will be precipitated. This can be filtered off. (Sm^{2+} and 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— SO_3H . The Ln^{3+} ions are absorbed onto the resin and replace the hydrogen atom on— SO_3H .



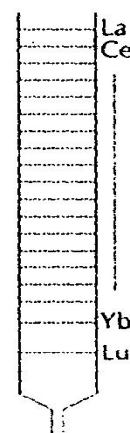
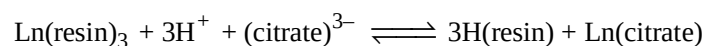
The individual salts are hydrated to varying degrees. Lutetium, being smallest, is most heavily hydrated, while lanthanum, being largest, is least hydrated.



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 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 $(\text{NH}_4)_3(\text{H} \cdot \text{EDTA})$ at pH 8. Consider the citrate case. An equilibrium is set up:



As the citrate solution flows down the column, Ln^{3+} ions are removed from the resin and form the citrate complex. A little lower down the column the 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 Lu^{3+} form stronger complexes with the citrate ions than do the larger ions like 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.

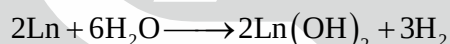
Chemical Properties of (+III) Compounds:

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.

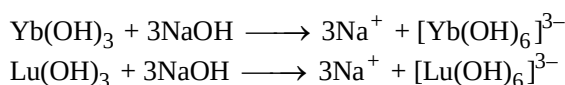
The sum of the first three ionization energies varies with minima at La^{3+} , Gd^{3+} and Lu^{3+} which are associated with attaining an empty, half full or full f shell. Maxima occur at Eu^{3+} and Yb^{3+} associated with breaking a half full or full shell.

The standard reduction potentials E° 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 is Al ($E^\circ = -1.66$ volts) and are slightly more reactive than Mg ($E^\circ = -2.37$ volts). Thus they react slowly with cold water, but more rapidly on heating.

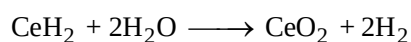


The hydroxides $\text{Ln}(\text{OH})_3$ are precipitated as gelatinous precipitates by the addition of NH_4OH to aqueous solutions. These hydroxides are ionic and basic. They are less basic than $\text{Ca}(\text{OH})_2$ but more basic than $\text{Al}(\text{OH})_3$ which is amphoteric. The metals, oxides and hydroxides all dissolve in dilute acids, forming salts. $\text{Ln}(\text{OH})_3$ are sufficiently basic to absorb 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 NaOH , forming complex.



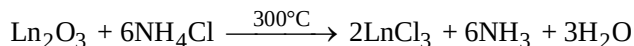
The metals tarnish readily in air, and on heating in O_2 they all give oxides Ln_2O_3 . Yb and Lu form a protective oxide film, which prevents the bulk of the metal forming the oxide unless it is heated to 1000°C . The one exception is Ce which forms $\text{Ce}^{\text{IV}}\text{O}_2$ rather than Ce_2O_3 . The oxides are ionic and basic. **Basic strength decreases as the ions get smaller.**

The metals react with H_2 , but often require heating up to 300 – 400°C to start the reaction. The products are solids of formula LnH_2 . Eu and Yb both have a tendency to form divalent compounds and EuH_2 and YbH_2 are salt-like hydrides and contain M^{2+} and two H^- . The other all form hydrides LnH_2 which are black, metallic and conduct electricity. These are better formulated as Ln^{3+} , 2H^- 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°C . They are decomposed by water, and react with oxygen.

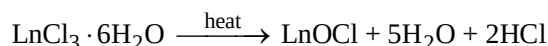


These 'dihydrides' take up H if heated under pressure, and all except Eu form salt-like hydrides LnH_3 made up of Ln^{3+} and three H^- . These do not have a delocalized electron, and do not show metallic conduction.

The anhydrous halides MX_3 can be made by heating the metal and halogen, or by heating the oxide with the appropriate ammonium halide.



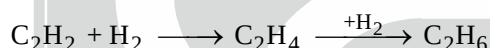
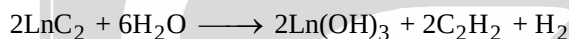
The fluorides are very insoluble, and can be precipitated from solutions of Ln^{3+} by addition of Na^+F^- or HF. This is used as a test for the lanthanides in qualitative analysis. However, with excess F^- , the smaller lanthanide ions may form soluble complexes $[\text{LnF}(\text{H}_2\text{O})_n]^{2+}$. 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.



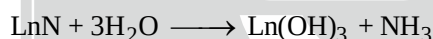
Heating $\text{CeX}_3 \cdot (\text{H}_2\text{O})_n$ results in CeO_2 . The bromides and iodides are similar to the chlorides.

At elevated temperatures, the lanthanides react with B, giving LnB_4 and LnB_6 .

On arc-melting the metals with C in an inert atmosphere they form carbides of stoichiometry LnC_2 and $\text{Ln}_4(\text{C}_2)_3$. The carbides can also be made by reducing Ln_2O_3 with C in an electric furnace. LnC_2 are more reactive than CaC_2 . They react with water, giving ethyne and also some hydrogen, C_2H_4 and C_2H_6 . They also show metallic conductivity. They do not contain $\text{Ln}(\text{+II})$ and are best described as acetylides of Ln^{3+} and C_2^{2-} -with the extra electron in a conduction band.

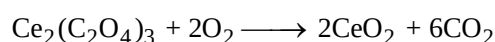
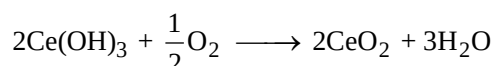
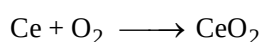


At elevated temperatures the metals also react with N, P, As, Sb and Bi, giving LnN etc. The latter is hydrolysed by water in a similar way to AlN :



Oxidation State (+IV):

The only (+IV) lanthanide which exists in solution and has any aqueous chemistry is 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 Ce^{4+} is hydrolysed, giving polymeric species and H^+ . $\text{Ce}(\text{+IV})$ solutions are widely used as an oxidizing agent in volumetric analysis instead of KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$. In classical analysis burettes containing 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 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 α -carbon atom. The common compounds are CeO_2 (white when pure) and $\text{CeO}_2 \cdot (\text{H}_2\text{O})_n$ (a yellow gelatinous precipitate). 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. CeO_2 has a fluorite type of structure. It is insoluble in acids and alkalis, but dissolves if reduced, giving Ce^{3+} solutions.



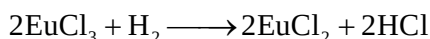
$\text{Ce}(\text{SO}_4)_2$ (formerly called ceric sulphate) is well known and is yellow like K_2CrO_4 . CeF_4 is obtained from CeF_3 and F_2 . It is white, and is rapidly hydrolysed by water. It has a three-dimensional crystal structure with the

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 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 Ph_3PO , 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.

Oxidation State (+II):

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

The most stable divalent lanthanide is Eu^{2+} . This is stable in water, but the solution is strongly reducing. $\text{Eu}^{\text{II}}\text{SO}_4$ can be prepared by electrolysis solutions, when the divalent sulphate is precipitated. $\text{Eu}^{\text{II}}\text{Cl}_2$ can be made as a solid by reducing $\text{Eu}^{\text{III}}\text{Cl}_3$ with H_2 .



Aqueous Eu^{3+} solutions can be reduced by Mg, Zn, zinc amalgam or electrolytically to give Eu^{2+} . EuH_2 is ionic and similar to CaH_2 . $\text{Eu}(\text{II})$ 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 NH_3 .

One major difference between Eu and Ca is that the dihalides 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.

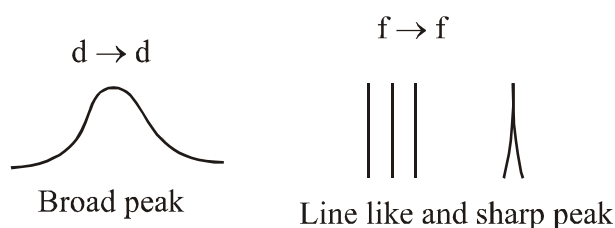
Yb^{2+} and Sm^{2+} can be prepared by electrolytic reduction of their trivalent ions; in aqueous solution. However, the Ln^{2+} ions are readily oxidized by air. These two elements form hydroxides; carbonates, halides, sulphates and phosphates.

The states $\text{Nd}(\text{+II})$, $\text{Pm}(\text{+II})$, $\text{Sm}(\text{+II})$ and $\text{Gd}(\text{+II})$ are only found in solid dihalides LnCl_2 and 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. $\text{Na}_2\text{SO}_4\text{Ln}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, 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.

Main smith colour sequence:

f^0, f^7, f^{14} are colourless

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

Ce³⁺ and Tb³⁺ transition 4f → 5d.

$$\Delta\ell = 1$$

Stronger absorption than forbidden f–f transitions. The electronic configuration of Ce³⁺ of f¹ and Yb³⁺ is f¹³, loss of one electron gives the extra stability of an empty or half full shell.

Ce⁴⁺ = Ligand → Metal charge transfer

Sm²⁺ = Metal → Ligand charge transfer

Tb³⁺ = f → d transition

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

SmH₂ → [SmH₂][−] conductor

Colour of (Lanthanide) Ln⁴⁺, Ln²⁺ and their isoelectronic Ln³⁺.

Ce ⁴⁺	Orange-red	4f ⁰	La ³⁺	Colourless
Sm ²⁺	Blood red	4f ⁶	Eu ³⁺	Pale Pink
Eu ²⁺	Pale greenish yellow	4f ⁷	Gd ³⁺	Colourless
Yb ²⁺	Yellow	4f ¹⁴	Lu ³⁺	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 Lu³⁺ 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^{−1}, 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 4*f* to the 5*d* level. Such transitions give broader peaks and their position is affected by the nature of the ligands.

Absorption spectral 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^{13} . 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 an 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. (μ_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 .

$$J = L - S \quad \text{when the shell is less than half full}$$

$$\text{and } J = L + S \quad \text{when the shell is more than half full}$$

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

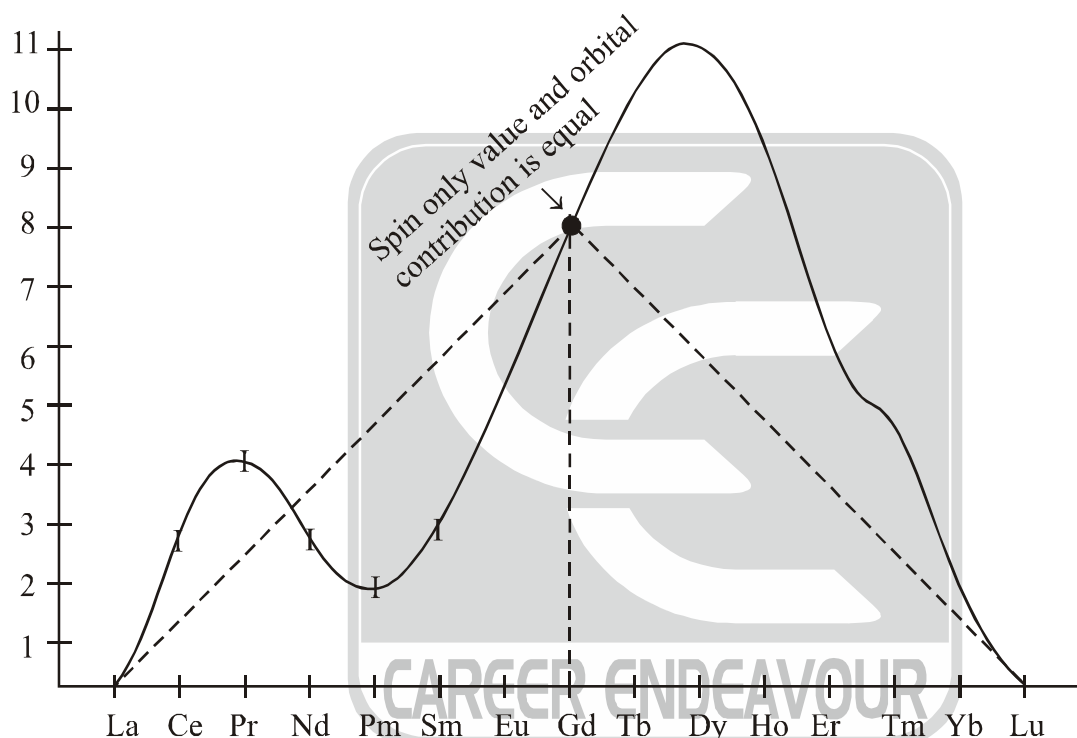
agreement between the calculated values using the coupled spin + orbital momentum formula and experimental values measured at 300 K. The range of experimental values are shown as bars.

The agreement for Eu^{3+} is poor, and that for Sm^{3+} is not very good. The reason is that with Eu^{3+} the spin orbit coupling constant is only about 300 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 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 ($J = L + S$).

La^{+3} and Lu^{+3} is diamagnetic

Ce^{+3} to Yb^{+3} is paramagnetic



Spin orbital coupling parameter
energy level are very small

5 —
4 —
3 —
2 —
1 —
J=0 —

7/2 — Sm^{+3}
5/2 — Pm^{+3}

gap is very small

Ce^{+3}

3 2 1 0 -1 -2 -3
4f¹

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

$2s + 1 = 2$

Ground state term of $\text{Ce}^{+3} = \boxed{{}^2\text{F}_{5/2}}$

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

Ground state term:

Magnetic property:

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

g = Lande's splitting factor.

or

gyromagnetic ratio.

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

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

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

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

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

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

calculated

observed

Config. Ground		No. of		Magnetic Moment [B.M.]		
Ln	M^{3+}	State term	unpaired e^-	Colour	calculated	observed
La	$4f^0$	${}^1\text{S}_0$	0	colourless	0	0
Ce	$4f^1$	${}^2\text{F}_{5/2}$	1	colourless	2.54	2.3 - 2.5
Pr	$4f^2$	${}^3\text{H}_4$	2	green	3.58	3.4 - 3.6
Nd	$4f^3$	${}^4\text{I}_{9/2}$	3	lilac	3.62	3.5 - 3.6
Pm	$4f^4$	${}^5\text{I}_4$	4	pink	2.68	-
Sm	$4f^5$	${}^6\text{H}_{5/2}$	5	yellow	0.85	1.4 - 1.7
Eu	$4f^6$	${}^7\text{F}_0$	6	pale pink	0	3.3 - 3.5
Gd	$4f^7$	${}^8\text{S}_{7/2}$	7	colourless	7.94	7.9 - 8.0
Tb	$4f^8$	${}^7\text{F}_6$	6	pale pink	9.72	9.5 - 9.8
Dy	$4f^9$	${}^6\text{H}_{15/2}$	5	yellow	10.65	10.4 - 10.6
Ho	$4f^{10}$	${}^5\text{I}_8$	4	yellow	10.6	10.4 - 10.7
Er	$4f^{11}$	${}^4\text{I}_{15/2}$	3	rose-pink	9.58	9.4 - 9.6
Tm	$4f^{12}$	${}^3\text{H}_6$	2	pale green	7.56	7.1 - 7.6
Yb	$4f^{13}$	${}^2\text{F}_{7/2}$	1	colourless	4.54	4.3 - 4.9
Lu	$4f^{14}$	${}^1\text{S}_0$	0	colourless	0	0