Lanthanides

General discussion:

- The f-block elements appear in two series characterized by filling of 4f and 5f orbitals. The series contains fourteen elements Cerium to Lutetium (Z = 58 – 71) and are called lanthanides as they appear after lanthanum. The second series Thorium to Lawrencium (Z = 90 – 103) appear after actinium and are called actinides.
- Lanthanide elements lie between lanthanum ($_{57}$La), an element of Group 3 and hafnium ($_{72}$Hf), the element of Group 4, both belonging to third transition series (or 5d-transition series). That is why they are also known as inner transition elements.
- These elements were originally called rare earth elements (REEs) because the elements then known to occurred as oxides (earths) and were available scarcely. Chemists of the past generally used the term ‘earth’ for many oxides. For example ‘alkaline earth’ for CaO, MgO etc.
- Electronic configuration and chemical properties of RREs are very close to each other which may be called a prototype of lanthanide elements. All these elements said to be the members of Group 3, i.e., Sc group and have been allotted one single position in the periodic table.
- The lanthanide elements with even atomic numbers are relatively more abundant and also have seven natural isotopes (except Er, 6 and Ce, 4 isotope) but those with odd atomic numbers are less abundant and have one natural isotopes (except Eu, Lu which have two).
- Abundance: Promethium (Pr) least abundant, 10^{-20} ppm; Cerium ($_{58}$Ce) most abundant, 60 ppm; the 2nd most abundant Neodymium ($_{60}$Nd), 40 ppm; Praseodymium ($_{59}$Pr), Samarium ($_{62}$Sm), Gadolinium ($_{64}$Gd) > 5 ppm; Thulium ($_{69}$Tm), 0.5 ppm; Lutetium ($_{71}$Lu), 0.8 ppm.
- Occurrence: Two most commercially important minerals are Monazite, a mixed phosphate of REEs and Bastnaesite, a fluoride carbonate of REEs.

Electronic Configuration:

The electronic configurations of the lanthanides were derived from the electronic spectra of the atoms of these elements. These spectra have great complexity thereby inferring to some doubt about the configurations. The expected configurations of lanthanum are that additional electrons are filled in 4f-subshell successively from cerium to lutetium. Thus, the 4f-electrons are embedded in the interior while 5d and 6s electrons are exposed to the surroundings.

But, it is evident that, the solitary 5d electron shifts into the 4f-subshell in all the cases except in Ce (58), Gd (64) and Lu (71) because it is favourable energetically to move the single 5d-electron into 4f-orbital in most of the elements. From the above, it may be concluded that the general electronic configuration of lanthanide elements could be written as $[Xe]_{54}\ 4f^{1\text{-}14}\ 5d^{0\text{-}1}\ 6s^2$. The three subshell that is, 4f, 5d and 6s together form the valence shell of these elements.

i) At Cerium (Ce), where the increase in effective nuclear charge after lanthanum (La) is not sufficient to stabilize the $4f^2 5d^0$ electron configuration compared to $4f^1 5d^1$, that means the nuclear charge is not sufficient to contract the 4f orbitals to lower the energy well below the 5d.

ii) Gadolinium (Gd) has $4f^7 5d^1$ configuration, which reflects the stability of the half filled 4f shell.

iii) Lutetium (Lu) has $4f^{14} 5d^1$ configuration, where the electron is added beyond the capacity of the 4f shell.

iv) The electron configuration of Ln^{3+} ions vary regularly from $4f^1$ for Ce^{3+} to $4f^{14}$ for Lu^{3+}

Sl no.	Elements Name	Symbol	Outer electron Configuration	
			Ground state	M^{3+} ion
1	Lanthanum	$_{57}La$	$[Xe]_{54}\ 5d^1\ 6s^2$	$[Xe]_{54}\ 4f^0$
2	Cerium	$_{58}Ce$	$[Xe]_{54}\ 4f^1\ 5d^1\ 6s^2$	$[Xe]_{54}\ 4f^1$
3	Praseodymium	$_{59}Pr$	$[Xe]_{54}\ 4f^3\ 6s^2$	$[Xe]_{54}\ 4f^2$
4	Neodymium	$_{60}Nd$	$[Xe]_{54}\ 4f^4\ 6s^2$	$[Xe]_{54}\ 4f^3$
5	Promethium	$_{61}Pm$	$[Xe]_{54}\ 4f^5\ 6s^2$	$[Xe]_{54}\ 4f^4$
6	Samarium	$_{62}Sm$	$[Xe]_{54}\ 4f^6\ 6s^2$	$[Xe]_{54}\ 4f^5$
7	Europium	$_{63}Eu$	$[Xe]_{54}\ 4f^7\ 6s^2$	$[Xe]_{54}\ 4f^6$
8	Gadolinium	$_{64}Gd$	$[Xe]_{54}\ 4f^7\ 5d^1\ 6s^2$	$[Xe]_{54}\ 4f^7$
9	Terbium	$_{65}Tb$	$[Xe]_{54}\ 4f^9\ 6s^2$	$[Xe]_{54}\ 4f^8$
10	Dysprosium	$_{66}Dy$	$[Xe]_{54}\ 4f^{10}\ 6s^2$	$[Xe]_{54}\ 4f^9$
11	Holmium	$_{67}Ho$	$[Xe]_{54}\ 4f^{11}\ 6s^2$	$[Xe]_{54}\ 4f^{10}$
12	Erbium	$_{68}Er$	$[Xe]_{54}\ 4f^{12}\ 6s^2$	$[Xe]_{54}\ 4f^{11}$
13	Thulium	$_{69}Tm$	$[Xe]_{54}\ 4f^{13}\ 6s^2$	$[Xe]_{54}\ 4f^{12}$
14	Ytterbium	$_{70}Yb$	$[Xe]_{54}\ 4f^{14}\ 6s^2$	$[Xe]_{54}\ 4f^{13}$
15	Lutetium	$_{71}Lu$	$[Xe]_{54}\ 4f^{14}\ 5d^1\ 6s^2$	$[Xe]_{54}\ 4f^{14}$

লা সে পর নট পাম সাম ইউ গুড তব দিয়ো হো অর তুম অব লিয়ো।

Isolation of Lanthanides: From Monazite:

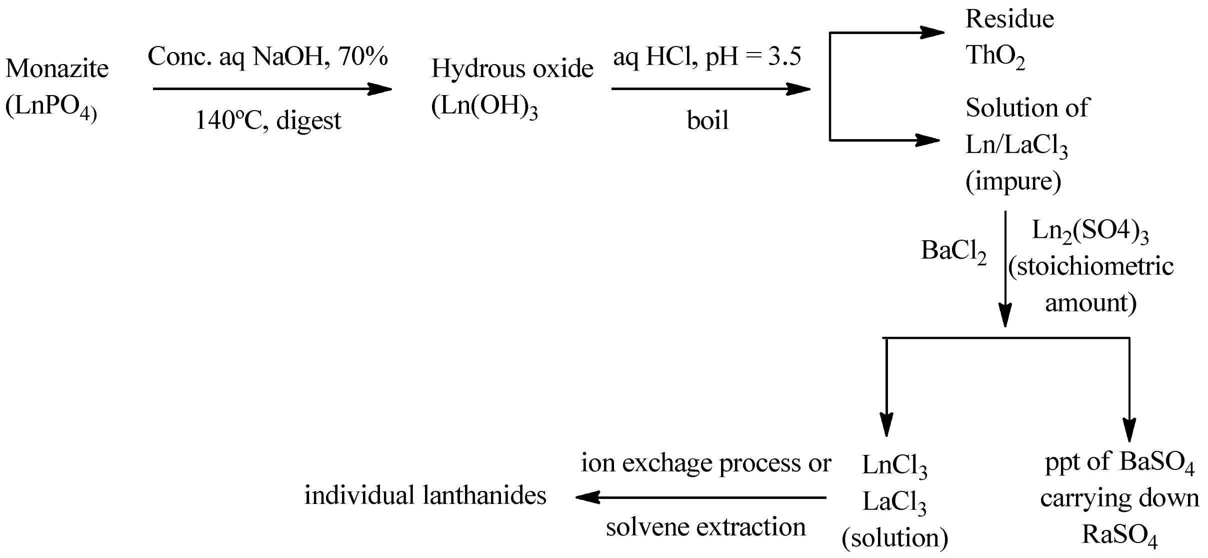
The main steps involved in obtaining a solution containing different rare earth element (Ln) are as follows:

(i) Digestion of the concentrated ore by concentrated aqueous NaOH (73%) at 140ºC, followed by extraction with water.

(ii) The slurry of impure hydrous oxide is boiled with HCl around pH = 3.5. ThO_2 (least basic) is precipitated and filtered out.

(iii) The filtrate containing $LaCl_3$ and $LnCl_3$ is treated with a solution of $BaCl_2$ and stoichiometric amount of $Ln_2(SO_4)_3$ to precipitate the entire barium as $BaSO_4$. The precipitated $BaSO_4$ carries with it traces of $RaSO_4$ (formed by 228-Ra, daughter of Th) and is removed by filtration.

(iv) The filtrate contains $LaCl_3$ and $LnCl_3$ from which lanthanum are separated by solvent extraction or ion exchange process.



Ion exchange Process: Separation of individual lanthanides from solution

As the size of the Ln^{3+} ion decreases gradually Ce^{3+} to Lu^{3+}, the binding of the Ln3+ ions to a complexing agent like EDTA gradually and regularly increases with increasing atomic number of REEs. The overall formation constant of $EDTA^{4-}$ complex of La^{3+} is $10^{15.3}$ and of Lu^{3+} is $10^{19.2}$. So, when a mixture of Ln3+ ions bound on an ion exchange bed (Dowex 50) is eluted with a dilute solution of EDTA then the rare earth ions will be eluted in a sequence from higher atomic number to lower atomic number, that is Lu^{3+} is eluted first followed by Yb^{3+} and so on.

First, a solution containing various Ln^{3+} ions run down a column of cation exchange resin as a result the Ln^{3+} ions are absorbed on the resin bed replacing the hydrogen from SO_3H group.

$3\ R\text{-}SO_3H + Ln^{3+} \rightarrow Ln(R\text{-}SO_3)_3 + 3H^+$

In the second step, Ln^{3+} ion are washed down or eluted from resin bed with $(NH_4)_3HEDTA$ at pH 8 or buffered solution of citric acid/ammonium citrate.

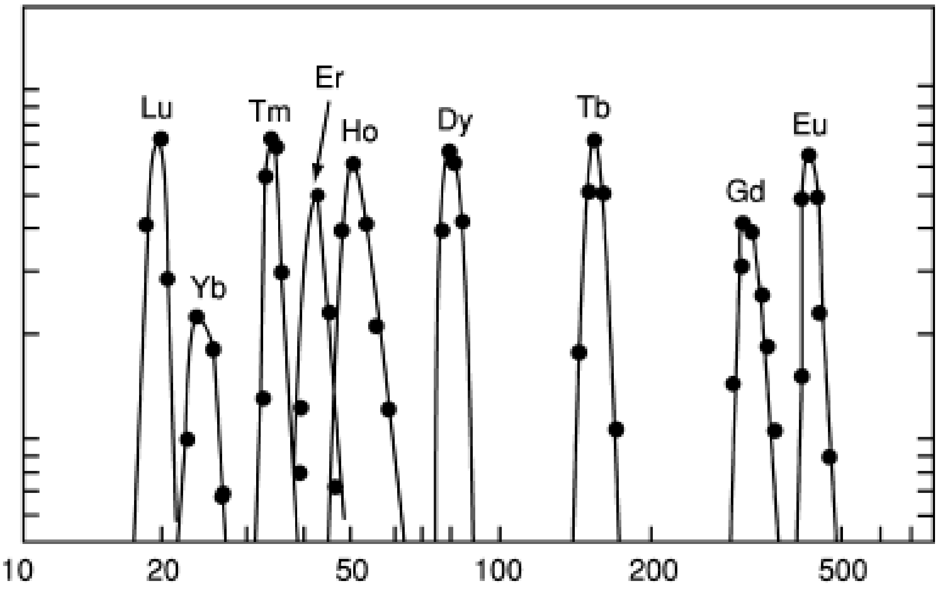
$Ln(R\text{-}SO_3)_3 + 3\ NH_4^+ + HEDTA^{3-} \rightarrow [Ln(H_2O)_xHEDTA] + 3\ R\text{-}SO_3^-NH_4^+$

As the heavier Ln3+ ions form stronger complexes with EDTA, they are gradually enriched in the solution phase and are eluted in the reverse order of their atomic number.

- The efficiency of the separation process may further increased by passing the Ln-EDTA complex solution through a second column charged with Cu^{2+} or Zn^{2+} on resin bed. The smaller Cu^{2+} ion on the resin bed is now displaced as the soluble $[HEDTA]^{3-}$ complex* while the Ln^{3+} ions are deposited on the resin bed. Now, the Ln^{3+} ion are again eluted from the resin bed with $[(NH_4)_3HEDTA]$ in succession.

* The concentration of the EDTA is kept below 0.015M, otherwise $Cu_2(EDTA)\cdot 5H_2O$ will be precipitated.

- From the solution obtained from ion-exchange column, lanthanides are precipitated as fluorides, oxalates or hydroxides. Oxalates and hydroxides compound yields oxides on heating. The oxides are again converted to chlorides by the action of ammonium chloride.



Volume of eluate (L) →

Lanthanide contraction

Among the post lanthanum elements of 4f-series, show a prominent steady decrease of the metallic radii as well as ionic radii (radii of tripositive ions, Ln^{3+}) this phenomenon is popularly referred to as lanthanide contraction.

The reason of this steady decrease in size lies primarily on the filling of the 4f subshell. In the f-series the differentiating electron goes to the second penultimate shell in the (n-2)f subshell. The f-orbitals have very much low screening power because of their diffused shape and also have least penetrating power into the inner electron core. So, successive electron additions to this subshell do not efficiently screen the next incoming electrons from the progressively increasing nuclear charge. Thus, with the gradual addition of the f electrons, the effective nuclear charge (Z*) experienced by the valence shell electrons gradually increases with the increase of atomic number along the series. This is why, contraction of spatial distribution of the orbitals and hence a gradual shrinkage in the atomic and ionic radii.

- The Relativistic effects on the 6s orbital of the lanthanides are also partly responsible for the lanthanide contraction.

Consequences of Lanthanide Contraction

a) Effect on the lanthanides

(i) Covalency increases from La(III) to Lu(III)

(ii) Basicity decreases from $La(OH)_3$ to $Lu(OH)_3$

(iii) Stability and tendency to form coordination compounds increases from La(III) to Lu(III)

(iv) Ionisation potential and standard reduction electrode potential of the M^{3+}/M couple increases from La to Lu.

(v) Thermal stability of oxy salts (e.g. carbonates, sulphates etc.) decreases from La(III) to Lu(III).

(ii) Basic character of lanthanide hydroxides, $Ln(OH)_3$:

Because the size of tripositive lanthanide ions (Ln^{3+}) decreases regularly with increasing atomic number (or nuclear charge), the process being called lanthanide contraction, therefore, the covalent character between Ln^{3+} ion and OH^- ions increases (ionic character decreases) from $La(OH)_3$ to $Lu(OH)_3$ according to the Fajans' rules. Therefore, tendency of dissociation to form OH^- in solution is decreases. As a result, the basic character of the hydroxides decreases with increasing atomic number. Consequently, $La(OH)_3$ is the most basic while $Lu(OH)_3$ is the least basic.

(iii) Stability and tendency to form coordination compounds

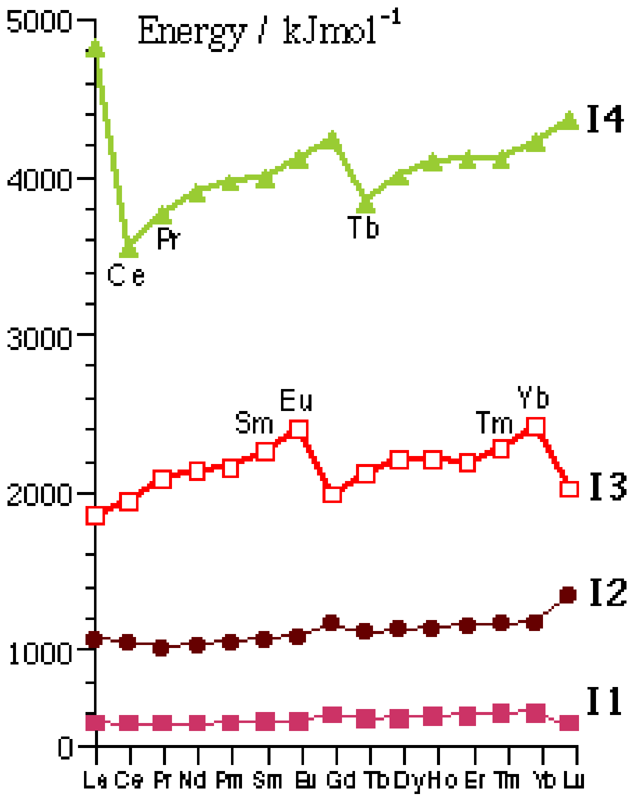
Since, the size of tripositive lanthanide ions (Ln^{3+}) decreases regularly with increasing atomic number (or nuclear charge), the ionic potential ($\varphi = \frac{\text{Charge}}{\text{radius}}$) is increases. Therefore, lanthanide cations with smaller size have greater binding with the hard anion compared to the larger lanthanide cations. So, stability and tendency to form coordination complex increases from La(III) to Lu(III).

(v) Thermal stability of oxy salts (e.g. carbonates, sulphates etc.)

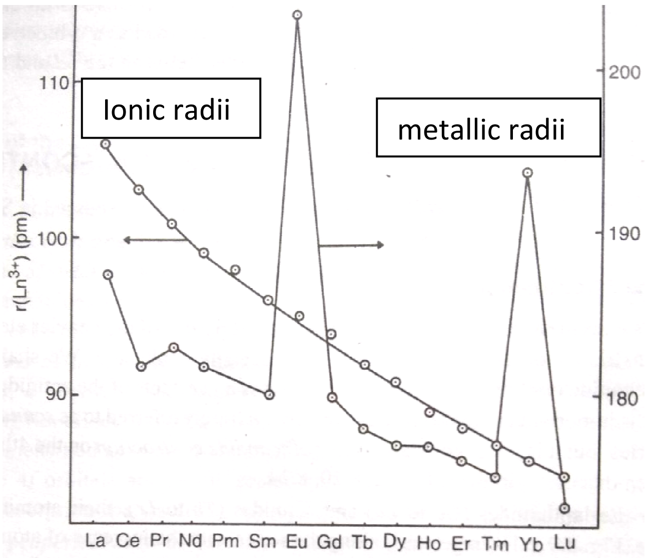
As we know, due to lanthanide contraction the ionic radii of Ln^{3+} are decreases gradually along the series. Therefore, Ln^{3+} having larger size bind effectively with larger anion like carbonates or sulfates compared to smaller Lu^{3+} ion, rather it form stable oxides. So, thermal stability of oxy salt decreases from La(III) to Lu(III).

Ionisation energy: Formation of Ln^{3+}

The ionisation energies of the lanthanides vary rather irregularly within the series. Several factors are involved in the process of ionisation, as the changing effective nuclear charge with varying shielding effect, the nature of the orbital involved, exchange energy, relativistic effect etc. It is seen that the characterized increase of the 3rd ionisation energy in a two step. In the first step, for La → Eu, each of the 4f orbitals of Ln^{II} ions are singly occupied and the stability of the 4f shell steadily increase due to the corresponding increase in nuclear charge. Then in the second step, for Gd → Lu, each 4f orbital is doubly occupied and vary the ionisation energy accordingly. The sudden falls at Gd and Lu reflects the case with which it is possible to remove the single electron in excess of the stable $4f^7$ and $4f^{14}$ configuration. It is also seen that there is sudden increase of 3rd ionisation energy for Eu and Yb, because electrons are removed from stable half filled or full filled shell.



Variation of ionisation energy



Variation ionic radii of Ln^{3+} ion and metallic radii

Oxidation state

Lanthanide elements are highly electropositive and form essentially ionic compounds. The chemistry of lanthanide is dominated by the +3 oxidation state (i.e. formation of tri-positive ions, Ln^{3+}) which is the principal or common and the most stable oxidation state of lanthanides. Some of these elements also show + 2 and +4 oxidation states but except a few such ions, they have the tendency to get converted to +3 state. The elements adjacent to lanthanum ($4f^0$), gadolinium ($4f^7$) and lutetium ($4f^{14}$) also exhibit other oxidation states.

- Ce ($4f^1\ 5d^1\ 6s^2$), Ce^{4+} is chemically accessible is due is to the high energy of the 4f orbitals at the start of the lanthanide. IV oxidation state of other lanthanides is not stable like Ce^{4+}.
- Eu ($4f^7\ 6s^2$), Yb ($4f^{14}\ 6s^2$), Eu^{2+} and Yb^{2+} are most stable II oxidation state which is accessible due to formation of stable $4f^7$ and $4f^{14}$ configuration.
- That is why Eu^{2+}, Yb^{2+} is a good reducing agent while Ce^{4+} is a good oxidising agent because they are easily converted to +3 states.
- $Eu^{2+} \rightarrow Eu^{3+} + e$; (electron provider, reducing agent)
- $Ce^{4+} + e \rightarrow Ce^{3+}$ (electron acceptor, oxidising agent)

One of the principal reasons for that is illustrated by the ionisation energy data which reveal that in all cases the fourth ionisation energy, I_4, is greater than the sum of first three ionisation energy. The extra energy required to remove the fourth electron is so large that in most cases it can’t be removed through chemical bond formation and thus +4 oxidation states is largely inaccessible. Therefore, the lanthanide metal shows stable +3 oxidation state.

- In this connection it is worth mentioning that, the valence electrons of the neutral lanthanide elements are distributed in the 4f, 5d and 6s orbitals. After removal of the valence electron from the neutral atom all the orbital are stabilized. But, 4f, 5d and 6s level do not experience the same degree of stabilization. 4f level is stabilized most while the 6s level stabilized least as the order of penetration of orbitals into the inner electron core decreases as 4f > 5d >6s. On successive ionisation the net charge on the lanthanide ion is increased the 4f electrons are affected most and the energy is lowered to the greatest extent than the 5d or 6s electron. Once three electrons have been removed the additional stabilization of the 4f orbitals over the 5d and 6s is so large that no electrons remain in these two orbitals. Furthermore remaining 4f electrons are so tightly held as to be chemically inaccessible.

Colour and spectral properties:

The excitation of an atom, ion or molecule from its ground state electronic level to higher energy level may be brought about by the absorption of electromagnetic radiation. Colours are produced when absorption of electromagnetic radiation in the visible region corresponding to the transition from ground to excited states. The substance shows complementary colour of the absorption.

Colourless		Coloured		
Ions	No. of 4f electron	Ions	No. of 4f electron	
La^{3+}	$4f^0$	Pr^{3+}, Tm^{3+}	$4f^2$, $4f^{12}$	Green
Ce^{3+}	$4f^1$	Nd^{3+}, Er^{3+}	$4f^3$, $4f^{11}$	Lilac (pale violet)
Gd^{3+}	$4f^7$	Pm^{3+}, Ho^{3+}	$4f^4$, $4f^{10}$	Pink, yellow
Yb^{3+}	$4f^{13}$	Sm^{3+}, Dy^{3+}	$4f^5$, $4f^9$	Yellow
Lu^{3+}	$4f^{14}$	Eu^{3+}, Tb^{3+}	$4f^6$, $4f^8$	Pale pink

Aqueous solutions of the most of the lanthanide ions are coloured, except when the ions have f^0, f^1, f^7, $f^{13}$and f^{14} configurations. It may be observed that ions with f^n and f^{14-n} configurations have similar colour. The colour arises due to f-f transitions, which are forbidden like d-d transition. 4f orbitals are radially much more contracted and deeply seated than d-orbitals of transition metals, to the extent that the filled 5s and 5p orbitals largely shield the 4f electron from the crystal field effect of the ligands. Hence, the intensities of the electronic transition are much weaker. As many of these electronic transition lie in the visible region of the electromagnetic spectrum, the colour of the Ln^{3+} compounds are typically less intense than those of the transition metal compound.

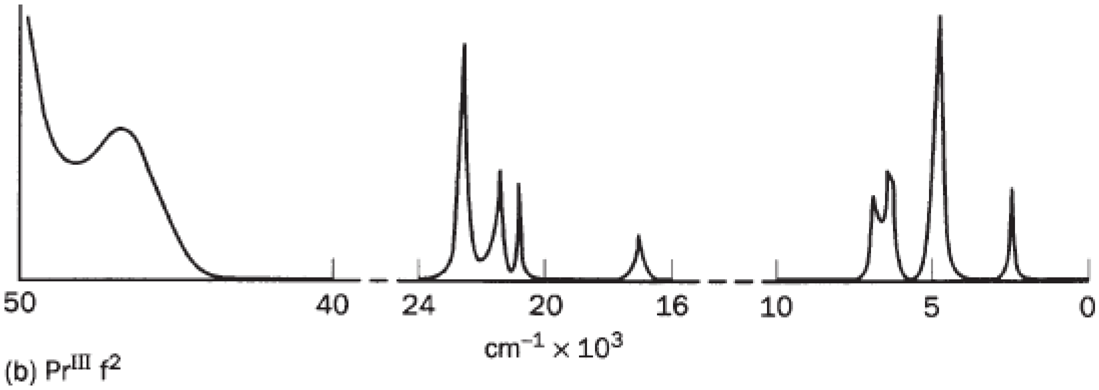
❖ The f-orbitals lie deep in the atom and are shielded from interference by the nature of the ligands or by thermal vibration. The bands arising from f-f transitions are thus sharp and much narrower.

❖ At the same time, spin orbit coupling for the lanthanides becomes more important than crystal field effects and states with different J values are sufficiently apart in energy. Thus electronic transition between them gives rise to sharp bands.

❖ Since the f electrons are practically unaffected by complex formation, hence colour remains almost constant for a particular ion regardless of the ligands or environments.

❖ The numbers of theoretically possible transitions are large, giving several peaks in the electronic spectrum.

❖ All lanthanide ions (except La^{3+} (f^0) and Lu^{3+} (f^{14}) show luminescence. Particularly Eu^{3+} (f^6) and Tb^{3+}(f^8) showing strong emissions. The origin of this phenomenon is f-f transition. For the luminescence properties lanthanide complexes used as phosphors on TV screens and fluorescent lighting.



(b) Pr^{III} f^2

Magnetic properties

Magnetism is a property associated with unpaired electrons. La^{3+} (f^0), Ce^{4+} (f^0), Yb^{2+} (f^{14}) and Lu^{3+}(f^{14}) have no unpaired electron, hence they are diamagnetic. Other lanthanide ions have unpaired electron in 4f orbital, so they are paramagnetic.

The observed magnetic moments of the Ln^{3+} ions do not follow the simple spin only formulae, $\mu = \sqrt{n(n+2)} = \sqrt{4S(S+1)}$ where n = no. of unpaired electron and S = spin quantum no. Magnetic behaviour of lanthanides arises due to the contribution of both spin moment and orbital magnetic moment, unlike the d-block elements. Because in case of inner-transition f-block elements, the 4f orbitals are quite shielded from the surroundings and do not interact strongly with the ligands surrounding the metal ion. Consequently, the orbital motions of 4f orbitals are not restricted (not quenched). Therefore, in case of lanthanides, the magnetic effect arising from the orbital motion of the electron, as well as that arising from the spin motion, contributes to the total magnetic moment. Thus, magnetic moments of lanthanides are calculated by taking into consideration spin as well as orbital contributions, $\mu = \sqrt{4S(S+1) + L(L+1)}$ is used, where L = orbital quantum no. and S = spin quantum no. In case of lanthanides, the spin contribution (S) and orbital contribution (L) couple together to give a new quantum no. J, called total angular momentum quantum no. where J = L-S, for less than half filled and J = L+S, for more than half filled.

Magnetic moment value in Bohr Magneton (B.M.) is given by: $\mu = g\sqrt{J(J+1)}$

Where g is called Lande splitting factor and is given by:

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Magnetic moments (B.M.) of Ln^{3+} ions

Ion	Electron configuration	Ground state	g	Magnetic moment		
				Spin only	$\mu = g\sqrt{J(J+1)}$	Observed
La^{3+}	$4f^0$	$^1S_0$	0	0.0	0.0	0.0
Ce^{3+}	$4f^1$	$^2F_{5/2}$	6/7	1.7	2.54	2.3-2.5
Pr^{3+}	$4f^2$	$^3H_4$	4/5	2.8	3.58	3.4-3.6
Nd^{3+}	$4f^3$	$^4I_{9/2}$	8/11	3.9	3.62	3.5-3.6
Pm^{3+}	$4f^4$	$^5I_4$	3/5	4.9	2.68	2.7
Sm^{3+}	$4f^5$	$^6H_{5/2}$	2/7	5.9	0.84	1.5-1.6
Eu^{3+}	$4f^6$	$^7F_0$	1	6.9	0.0	3.4-3.6
Gd^{3+}	$4f^7$	$^8S_{7/2}$	2	7.9	7.94	7.8-8.0
Tb^{3+}	$4f^8$	$^7F_6$	3/2	6.9	9.72	9.4-9.6
Dy^{3+}	$4f^9$	$^6H_{15/2}$	4/3	5.9	10.63	10.4-10.5
Ho^{3+}	$4f^{10}$	$^5I_8$	5/4	4.9	10.60	10.3-10.5
Er^{3+}	$4f^{11}$	$^4I_{15/2}$	6/5	3.9	9.58	9.4-9.6
Tm^{3+}	$4f^{12}$	$^3H_6$	7/6	2.8	7.56	7.1-7.4
Yb^{3+}	$4f^{13}$	$^2F_{7/2}$	8/7	1.7	4.54	4.4-4.9
$_{71}Lu$	$4f^{14}$	$^1S_0$	1	0.0	0.0	0.0

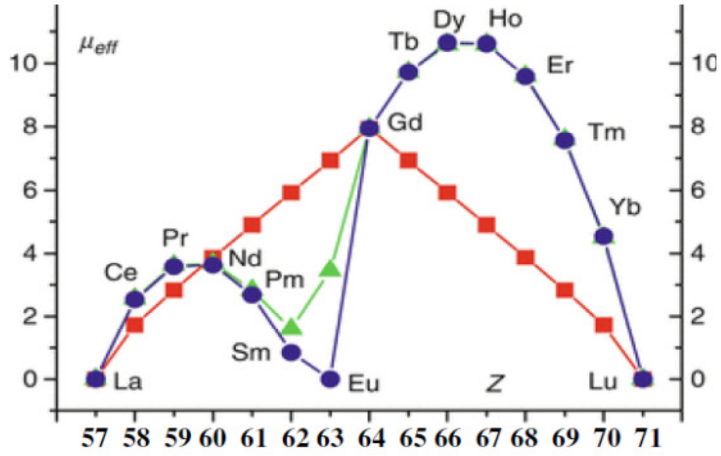
Magnetic moment of Sm^{III} and Eu^{III} differ from calculated value by using formula $\mu = g\sqrt{J(J+1)}$. Why?

Sm^{III} and Eu^{III} stand notable exceptions from the general agreement found in other lanthanide ions. The spin orbit coupling constant (λ) and the energy separation between the ground state and first excited states (ΔE) for these ions are small comparatively.

For Sm^{3+}, $\lambda = 240$ cm^{-1} and $\Delta E = 7/2\lambda$ while for Eu^{3+}, $\lambda = 230$ cm^{-1} and $\Delta E = \lambda$

The lower value of ΔE compared with the value of thermal energy (kT) ~200 cm^{-1} at ordinary temperature leads the first excited state of Sm^{3+} and first two or three excited states of Eu^{3+} will be populated. Mixing of these states with higher J values causes the observed magnetic moment to be higher than expected from spin orbit coupling moment.

Variation of Magnetic moments of Ln^{3+} ions:



Spin only Observed Calculated, $g\sqrt{J(J+1)}$

Calculation of magnetic moment : f^5 configuration:

m_l	+3	+2	+1	0	-1	-2	-3	$L = \Sigma m_l = 3+2+1-1 = 5$
	↑	↑	↑	↑	↑			$S = \Sigma m_s = 5/2$; Spin multiplicity (2S+1) = [(2 x 5/2) + 1] = 6

L	0	1	2	3	4	5	6
State	S	P	D	F	G	H	I

$J = |L + S|$ to $|L - S|$

So, J = (5 + 5/2) to (5-5/2) = 15/2 to 5/2.

Since it is less than half filled J will be 5/2.

Therefore, Term symbol for f^5 will be $(^{2S+1}L_J)$ $^6H_{5/2}$.

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} = \frac{3}{2} + \frac{5/2(5/2+1) - 5(5+1)}{2 \text{ x } 5/2(5/2+1)} = \frac{3}{2} + \frac{(\frac{5}{2} \text{x} \frac{7}{2}) - (5 \text{ x } 6)}{2 \text{ x} \frac{5}{2} \text{x} \frac{7}{2}}$$

$$= \frac{3}{2} + \frac{\frac{35}{4} - 30}{\frac{35}{2}} = \frac{3}{2} + \frac{\frac{35-120}{4}}{\frac{35}{2}} = \frac{3}{2} + \frac{\frac{-85}{4}}{\frac{35}{2}} = \frac{3}{2} + \left(-\frac{85}{4} \text{x} \frac{2}{35}\right) = \frac{3}{2} - \frac{17}{14} = \frac{21-17}{14} = \frac{2}{7}$$

Magnetic moment, $\mu = \frac{2}{7}\sqrt{\frac{5}{2}(\frac{5}{2}+1)} = \frac{2}{7}\sqrt{35/4} = \frac{2}{7}\sqrt{35/4} = 0.285 \text{ x } 2.958 = 0.84$

f^8 configuration:

m_l	+3	+2	+1	0	-1	-2	-3	$L = \Sigma m_l = 3+3+2+1-1-2-3 = 3$
	↑↓	↑	↑	↑	↑	↑	↑	$S = \Sigma m_s$ = (6 x ½) = 3; Spin multiplicity (2S+1) = [(2 x 3) + 1] = 7

$J = |L + S|$ to $|L - S|$; So, J = (3 + 3) to (3 - 3) = 6 to 0.

Since it is more than half filled J will be 6.

Therefore, Term symbol for f^5 will be $(^{2S+1}L_J)$ $^7F_6$.

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} = \frac{3}{2} + \frac{3(3+1) - 3(3+1)}{2 \text{ x } 6(6+1)} = \frac{3}{2} + \frac{(3\text{x } 4) - (3 \text{ x } 4)}{2 \text{ x } 6\text{x } 7}$$

$$= \frac{3}{2} + \frac{12 - 12}{84} = \frac{3}{2} + 0 = \frac{3}{2}$$

Magnetic moment, $\mu = \frac{3}{2}\sqrt{6(6+1)} = \frac{3}{2}\sqrt{35/4} = \frac{3}{2}\sqrt{42} = 1.5 \text{ x } 6.48 = 9.72$

Actinides

General discussion:

- The group of fourteen elements from thorium (Th, Z = 90) to lawrencium (Lr, Z=103) are called actinides, actinoids or actinons. These are named so because these elements are after actinium (Ac, Z = 89).
- These elements are also known as inner-transition elements as they lie between actinium (Gr. 3) and rutherfordium (Rf, Z =104) (Gr. 4). Thus, they constitute the second inner-transition series of which actinium is the prototype.
- In these elements 5f-subshell of the second penultimate shell (n=7) is successively filled by the additional or differentiating electrons, one at a time in each step, which are embedded in the interior while 6d- and 7s-electons are exposed to the surroundings.
- In the outermost and penultimate shell of these elements, the number of electrons remains almost the same. That is why the actinides resemble one another very closely.
- The actinides lying beyond uranium, i.e., the elements with Z = 93 to 103 are called trans-uranium elements.
- All of them are radioactive, but the most abundant isotopes of thorium and uranium have very long half lives (^{232}Th: 1.4×10^{10} y and ^{238}U: 4.5×10^{9} y).
- Except actinium, thorium, protactinium and uranium, all in this series are synthetic.

Electronic Configuration:

The electronic configuration of actinium (Z = 89) which is followed by fourteen actinides is $[Rn]_{86}\ 5f^0 6d^1 7s^2$, the last electron entering the 6d-subshell. In the next element, Th, the first member of the actinide series, the additional electron must enter 5f-subshell and the filling of 5f-subshell must continue progressively till the last element, Lr. Thus, 6d-subshell in all the elements must remain singly filled thereby giving the expected valence shell configuration of $[Rn]5f^{1-14}6d^1 7s^2$ for these elements. Since, the energies of 6d- and 5f- subshell are almost the same and the atomic spectra of the elements are very complex, it is difficult to identify the orbital in terms of quantum numbers as well as to write down the configuration. For chemical behaviour, the valence shell electronic configuration of the elements is of great importance and the competition between $5f^n 6d^0 7s^2$ and $5f^{n-1} 6d^1 7s^2$ is of interest. It has been observed that the electronic configuration of actinides does not follow the simple pattern as is observed for the lanthanides. For the first four actinide elements, viz., Th, Pa U and Np, due to almost equal energies of 5f and 6d, the electrons may occupy the either 5f or 6d subshell or sometimes both. From Pu (Z=94) onwards, $6d^1$ electron gets shifted to 5f-subshell except for Cm (Z=96) and Lr (Z=103) in which $6d^1$ electron does not shift to 5f due to stable $5f^7$ and $5f^{14}$ configurations. In view of the above considerations, the general valence shell electronic configuration of the actinide elements may be written as: $[Rn]_{86}\,5f^{0-14}6d^{0-2}7s^2$. For individual elements the observed or actual valence shell configurations are listed below:

Sl no.	Elements Name	Symbol	Outer electron Configuration	Radii (pm)		Configuration An^{3+}
				metallic	An^{3+}	
1	Actinium	$_{89}Ac$	$[Rn]_{86}\,6d^1\,7s^2$	190	108	$5f^0$
2	Thorium	$_{90}Th$	$[Rn]_{86}\,5f^0\,6d^2\,7s^2$	180	104	$5f^1$
3	Protactinium	$_{91}Pa$	$[Rn]_{86}\,5f^2\,6d^1 7s^2$ $[Rn]_{86}\,5f^1\,6d^2 7s^2$	164	103	$5f^2$
4	Uranium	$_{92}U$	$[Rn]_{86}\,5f^3\,6d^1 6s^2$	154	102	$5f^3$
5	Neptunium	$_{93}Np$	$[Rn]_{86}\,5f^4\,6d^1 6s^2$ $[Rn]_{86}\,5f^5\,6d^0 7s^2$	150	101	$5f^4$
6	Plutonium	$_{94}Pu$	$[Rn]_{86}\,5f^6\,7s^2$	152	100	$5f^5$
7	Americium	$_{95}Am$	$[Rn]_{86}\,5f^7\,7s^2$	173	97.5	$5f^6$
8	Curium	$_{96}Cm$	$[Rn]_{86}\,5f^7\,6d^1\,7s^2$	174	96	$5f^7$
9	Berkelium	$_{97}Bk$	$[Rn]_{86}\,5f^9\,7s^2$ $[Rn]_{86}\,5f^8\,6d^1 7s^2$	170	95.5	$5f^8$
10	Californium	$_{98}Cf$	$[Rn]_{86}\,5f^{10}\,7s^2$	170	94	$5f^9$
11	Einsteinium	$_{99}Es$	$[Rn]_{86}\,5f^{11}\,7s^2$	169	93	$5f^{10}$
12	Fermium	$_{100}Fm$	$[Rn]_{86}\,5f^{12}\,7s^2$	194	92	$5f^{11}$
13	Mendelevium	$_{101}Md$	$[Rn]_{86}\,5f^{13}\,7s^2$	194	91	$5f^{12}$
14	Nobelium	$_{102}No$	$[Rn]_{86}\,5f^{14}\,7s^2$	194	90	$5f^{13}$
15	Lawrencium	$_{103}Lr$	$[Rn]_{86}\,5f^{14}\,6d^1\,7s^2$	171	89	$5f^{14}$

Radius for An^{3+} for Coordination number 6

Oxidation states

Though the general chemical behaviour of the actinides follows the trend set by the lanthanides, there are certain differences because of the smaller difference in energy between the 5f and 6d orbitals than the 4f and 5d orbitals. This is particularly true at the beginning of the series; later, however, the 5f orbitals become more stable as shown by the ground electron configuration of the elements. The An^{3+} and An^{4+} cations have the general $5f^n$ configuration. Poor shielding by the 5f orbitals and consequent rise in effective nuclear charge along the series give rise to a decrease in ionic radii.

Unlike the lanthanides, actinides offer a number of characteristic oxidation states, at least two oxidation states being found for most actinides. This may arise due to proximity in successive ionisation energies, but for the higher oxidation states, where covalent bonding is more likely, other factor need to consider. The 5f orbitals have a longer spatial extension than the 4f orbitals and can participate better in covalent bonding. Since, the energy of the 5f, 6d as well as 7s and 7p orbitals are comparable and the orbitals also overlap spatially, boding can involve any or all of them. At the same time, since the energy of these orbital are comparable so energy requirement for shifting of electron between the orbital may often in the range of chemical bonding energy. The lighter elements up to Am show variable oxidation states, the maximum being for Np, Pu and Am, but the heavier elements show oxidation state of +2 or +3. The important oxidation states exhibited by actinides are listed below. Some of them are stable but most of these oxidation states are unstable.

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

- The +3 oxidation state is exhibited by all the elements and it becomes more and more stable as the atomic number increases.
- The +2 oxidation state is shown by Th and Am only in the few compounds like $ThBr_2$, ThI_2, ThS, AmX_2 (X = Cl, Br, I) etc.
- The dipositive state becomes important for the later actinides. Their stability order is increases as $Cf^{2+} < Es^{2+} < Fm^{2+} < Md^{2+} << No^{2+}$. Thus, II state of nobelium is most stable.

- The +4 oxidation state is shown by the elements from Th to Cf,
- The +5 oxidation state is shown by Pa to Am.
- The +6 state is observed for the elements from U to Am.
- The +7 state is exhibited by only two elements, viz., Np and Pu. Np in the +7 state acts as an oxidising agent.
- The principal cations given by actinide elements are An^{3+}, An^{4+} and oxo-cations such as AnO_2^+ (oxidation state of An = +5) and AnO_2^{2+} (oxidation state of An = +6). The examples of oxo-cations are UO_2^+, PuO_2^+, UO_2^{2+} and PuO_2^{2+} which are stable in acid and aqueous solutions. Most of the An^{3+} ions are more or less stable in aqueous solution. Np^{3+} and Pu^{3+} ions in solution are oxidized to Np^{4+} and Pu^{4+} by air. The latter ions are further oxidized slowly to UO_2^{2+} and PuO_2^{2+} by air.

Magnetic and spectral properties

Actinides are second f-series element, it is expecting similarities with lanthanides in their magnetic and spectroscopic properties. But, it is more difficult to interpret the spectra and magnetic behaviour of actinide compounds than those of lanthanide compounds. The reasons is spin–orbit coupling plays a more important role in actinide chemistry as the longer spatial extension 5f orbitals and their electrons are not so 'core-like' as the 4f, particularly in the early part of the actinide series. This means that J is no longer such a good quantum number (Obtained from Russell–Saunders (RS) coupling scheme, which treats spin–orbit coupling as being much weaker than inter-electronic repulsion terms). Neither however, can one apply the other extreme, the j–j coupling scheme, which relies on spin–orbit coupling being strong compared with electrostatic repulsion. Thus the 'intermediate' coupling scheme (intermediate between RS and jj) is used to explain the magnetic and spectral properties of actinides. It is also noted that 5f and 6d-subshalls are sufficiently close in energy for the lighter actinides to make 6d levels accessible. This must allow the mixing of J levels obtained from Russel-Saunders coupling and population of thermally accessible excited levels. Accordingly, the expression $\mu = g\sqrt{J(J+1)}$ is less applicable for the actinides. Actually, magnetic moment values are usually lower due to quenching of orbital contribution by crystal field effect and are much more temperature dependent. Tetra-valent thorium (Th^{4+}) and hexa-valent uranium (U^{6+}) ions have no unpaired electrons and hence are diamagnetic.

Spectral properties:

The spectra of actinide ions are sensitive to the crystal field effects and may change from one compound to another. It is not possible to deduce the stereochemistry of actinide compounds due to complexity of the spectra. Most of the actinide cations and salts are coloured due mainly to f-f transitions but there are certain differences from spectra of lanthanides. Those with f^0, f^7 and f^{14} configurations are colourless.

(a) **f-f transitions**:

The f–f electronic transitions in the spectra of actinide complexes are relatively strong in comparison with those of lanthanides. Because, in the case of the actinides, the 5f orbitals are larger than lanthanide 4f orbitals, so that they interact more with ligand orbitals, causing much higher extinction coefficients and also, because covalency is greater, to create greater nephelauxetic effects in actinide spectra. This means that there is more variation in both position and intensity of absorption bands than in lanthanide compounds.

The Laporte forbidden 'f-f' transitions are relaxed partially by the action of crystal field or by an asymmetric ligand field, which introduce a permanent distortion or temporary coupling with an asymmetric metal–ligand vibration (vibronic coupling). Because of that observed absorption bands are broader, more intense and more dependent on ligands than in case of lanthanides. Generally, absorption occurs in the visible and UV regions and produce the colours.

5f-6d transitions:

These are Laporte and spin allowed transitions and give rise to much more intense bands which are broader than the f–f transitions, occur above 20000 cm^{-1}. In the case of the free U^{3+} ion, the $5f^26d^1$ level is over 30000 cm^{-1} above the $5f^3$ ground state, while in $U^{3+}(aq)$ the charge-transfer transitions start around 24 000 cm^{-1}. Thus, solvation has a very significant effect upon the relative energies of the 5f and 6d electrons.

Metal to ligand charge transfer: These transitions are also fully allowed and produce broad, intense absorptions usually found in UV region, sometimes trailing in the visible region and is responsible for the red, brown, or yellow colours often noted for actinide complexes with polarisable ligands like Br or I.

Similarities between lanthanides and actinides

(i) In both, lanthanides and actinides differentiating electron enters (n-2)f-subshell.

(ii) They exhibit +3 oxidation state as a stable and principal oxidation state.

(iii) Like lanthanide contraction, actinide contraction is also observed. Both the contractions are due to poor shielding effect of f-electron with increasing nuclear charge.

(iv) The electronic absorption bands are due f-f transitions.

(vi) Most of the lanthanide and actinide cations are paramagnetic.

(vii) The nitrates, perchlorates and sulphates of trivalent lanthanide and actinide elements are soluble while the hydroxides, fluorides and carbonates of these elements are insoluble.

(viii) The lanthanide and actinide elements show similarity in properties among their series though the lanthanides are closer among themselves in properties as compared to actinides.

Differences between lanthanides and actinides

i) The decrease of ionic radii (Ln^{3+}) and atomic radii follow a general trend with increase in atomic number in case of lanthanides whereas in case actinides, the decrease of both the atomic size and ionic radius (An^{3+}) is not so regular.

ii) Lanthanides mainly show +3 oxidation state along with +2 and +4 oxidation states in few cases but for actinides long with +3 oxidation state, +2, +4, +5, +6 and +7 oxidation state are also observed.

iii) Lanthanide compounds are less basic whereas actinide compounds are more basic.

iv) Lanthanides do not form oxo-cations but actinide form oxo-cations.

v) Lanthanides do not form complexes easily while actinides have greater tendency to form complexes

vi) Lanthanides are non-radioactive except Pm but all actinides are radioactive.

vii) Magnetic moment of lanthanide ions finely explained by LS coupling but for actinides both spin orbit coupling and ligand field effects have to be considered.

viii) In case of actinides effect of crystal field on spectral properties is more compared to lanthanide.