

"Chemistry of Lanthanoids & Actinoids"

← 'f'-block elements →

	(4f)	58	59	60	61	62	63	64	65	66	67	68	69	70	71
(4f) Lanthanide	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
	(5f)	90	91	92	93	94	95	96	97	98	99	100	101	102	103
(5f) Actinide ser.	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

1. Introduction :→ The fourteen elements from Cerium (Ce) to Lutetium (at. numbers 58 to 71) are called lanthanides or rare earths. These elements involve the filling of 4f orbitals. strictly speaking, the first member lanthanum (conf. $6s^2, 5d^1, 4f^0$) and the last member, lutetium ($6s^2, 5d^1, 4f^{14}$) have no partially filled 4f orbital in their ground state yet they are considered to belong to lanthanide series, because their chemical properties are very closely similar to the other 13 elements of the series.

These elements are also ~~also~~ called the inner transition elements, because the filling of e^- takes place in the 4f subshell, i.e., two levels below the outer 5p & 6s subshells which are already filled in these elements. the properties of lanthanides are very similar to one another & do not show much variations. Decrease in their radii as we move across from left to right such that La to Lu is responsible for small variation in their properties.

2. Electronic configuration of lanthanides :→ In lanthanum (57) the incoming e^- enters the 5d subshell & therefore it has the configuration $[Xe] 6s^2, 5d^1, 4f^0$. However, as we move one step further, the 4f subshell f.t.s

Teacher's Signature : _____

becomes more stable than the 5d subshell & the next e^- in Cerium enters the 4f subshell. Cerium has the configuration $[Xe] 6s^2, 4f^1, 5d^1$. The filling of 4f subshell continues till we reach ytterbium which has the configuration $[Xe] 6s^2, 4f^{14}, 5d^0$. Now after 6s & 4f subshells have been filled, the 5d subshell is the next choice for filling e^- . At lutetium the e^- enters the 5d subshell & it has the configuration $[Xe] 6s^2, 5d^1, 4f^{14}$. The electronic configuration & oxidising (oxidation) states of lanthanides are listed in table (in ~~last~~ page). In general, their configuration may be written as $[Xe] 6s^2, 4f^{0-14}, 5d^{0-1}$.

Table :- Configuration of Lanthanides

At. No.	ELEMENT NAME	SYMBOL	CONFIGURATION		Outer Configuration of			Oxidation state
			PROBABLE	OBSERVED	$M^{2+}[6s^0]$	$M^{3+}[6s^0]$	$M^{4+}[6s^0]$	
57	Cerium	La	$5d^1 6s^2 4f^0$	$4f^0 5d^1 6s^2$	$4f^0 5d^1$	$4f^0 5d^0 6s^0$	—	+3
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^1 5d^1 6s^2$	$4f^1 5d^1$	$4f^1 5d^0 6s^0$	$4f^0 5d^0 6s^0$	+3, +4
59	Praseodymium	Pr	$4f^2 5d^1 6s^2$	$4f^3 5d^0 6s^2$	$4f^3 5d^0$	$4f^2 5d^0 6s^0$	$4f^1$ "	+3, +4
60	Neodymium	Nd	$4f^3 5d^1 6s^2$	$4f^4 5d^0 6s^2$	$4f^4 5d^0$	$4f^3 5d^0 6s^0$	$4f^2$ "	+2, +3
61	Promethium	Pm	$4f^4 5d^1 6s^2$	$4f^5 5d^0 6s^2$	$4f^5 5d^0$	$4f^4$ —	$4f^3$ "	+3
62	Samarium	Sm	$4f^5 5d^1 6s^2$	$4f^6 5d^0 6s^2$	$4f^6 5d^0$	$4f^5$ —	$4f^4$ "	+2, +3
63	Europium	Eu	$4f^6 5d^1 6s^2$	$4f^7 5d^0 6s^2$	$4f^7 5d^0$	$4f^6$ —	$4f^5$ "	+2, +3 *
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7 5d^1 6s^2$	$4f^7 5d^1$	$4f^7$ —	$4f^6$ "	+3
65	Terbium	Tb	$4f^8 5d^1 6s^2$	$4f^9 5d^0 6s^2$	$4f^9 5d^0$	$4f^8$ —	$4f^7 6s^0$	+3, +4
66	Dysprosium	Dy	$4f^9 5d^1 6s^2$	$4f^{10} 5d^0 6s^2$	$4f^{10} 5d^0$	$4f^9$ —	$4f^8 6s^0$	+3, +4
67	Holmium	Ho	$4f^{10} 5d^1 6s^2$	$4f^{11} 5d^0 6s^2$	$4f^{11} 5d^0$	$4f^{10}$ —	—	+3
68	Erbium	Er	$4f^{11} 5d^1 6s^2$	$4f^{12} 5d^0 6s^2$	$4f^{12} 5d^0$	$4f^{11}$ —	—	+3
69	Thulium	Tm	$4f^{12} 5d^1 6s^2$	$4f^{13} 5d^0 6s^2$	$4f^{13} 5d^0$	$4f^{12}$ —	—	+2, +3
70	Ytterbium	Yb	$4f^{13} 5d^1 6s^2$	$4f^{14} 5d^0 6s^2$	$4f^{14} 5d^0$	$4f^{13}$ —	—	+2, +3
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14} 5d^1 6s^2$	$4f^{14} 5d^1$	$4f^{14}$ —	—	+3

3. Oxidation State:- The common oxidation state shown by all the lanthanides is +3. Some elements display +2 & +4 states, but these are always less stable than the group valency +3. The unusual oxidation states such as +2 or +4 exhibited by the lanthanides can be explained on the basis of extra stability associated with empty, half-filled or fully filled 4f subshell. Some examples are as follows:-

(i) Eu & Yb exhibit +2 oxidation states:- This is because in +2 oxidation states Europium & Ytterbium acquire f^7 & f^{14} electronic configuration as:-

$$\text{Eu}^{2+} : [\text{Xe}]4f^7, \text{Yb}^{2+} : [\text{Xe}]4f^{14}$$

(ii) Ce & Tb exhibit +4 oxidation states:- This is because in +4 oxidation state Cerium & Terbium acquire f^0 & f^7 electronic configuration which are supposed to be stable configurations.

$$\text{Ce}^{4+} : [\text{Xe}]4f^0, \text{Tb}^{4+} : [\text{Xe}]4f^7$$

(iii) La, Gd & Lu exhibit +3 oxidation states:- This is because in +3 oxidation states but La^{3+} has $[\text{Xe}]4f^0$, $\text{Gd}^{3+} : [\text{Xe}]4f^7$ & Lu^{3+} has $[\text{Xe}]4f^{14}$ electronic configurations which are stable due to empty, half-filled, or fully-filled 4f subshell respectively.

4. Exceptions:- There are few elements which show +2 & +4 oxidation states but their existence can't be easily justified.
 e.g.:- Sm & Tm show +2 state having f^6 & f^{13} e^- , when they are only one e^- short of the necessary half-filled or completely filled configuration. Other examples for +4 state even though they are left with f^1 & f^2 e^- oxidation states shown in table.

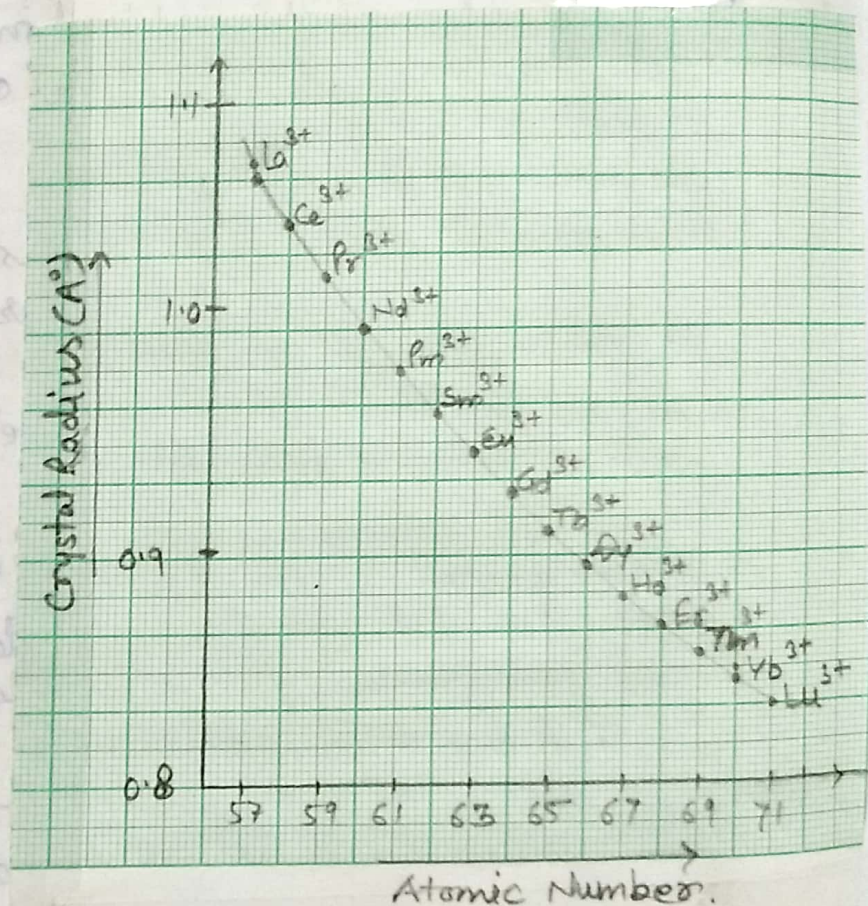
Teacher's Signature : _____

Lanthanide Contraction :- According to table & figure we find that as we move along the lanthanide series from La to Lu. there is a continuous decrease in the size of Lanthanide ion with increase in atomic number. This decrease is known as 'Lanthanide Contraction'. it ~~may~~ it may be define as the small steady decrease in size of Lanthanide ions with increase in atomic no.

Thus in the lanthanide series, La has the largest radius while Lu has the smallest radius.

Table:- Ionic Radii

At. No.	Element	Radius (in Å°)
57	La	1.15 Å°
58	Ce	1.11
59	Pr	1.09
60	Nd	1.08
61	Pm	1.06
62	Sm	1.04
* 63	Eu	1.02
64	Gd	1.00
65	Tb	0.99
66	Dy	0.97
67	Ho	0.96
68	Er	0.95
69	Tm	0.94
70	Yb	0.94
71	Lu	0.93



In moving Ce^{3+} to Lu^{3+} , $14e^-$ are added to $4f$ orbital, while the decrease in ionic radius is from (103 pm) to (85 pm) i.e. 18 pm only. This is a very small decrease in ~~comp~~ comparison to elements of other periods.

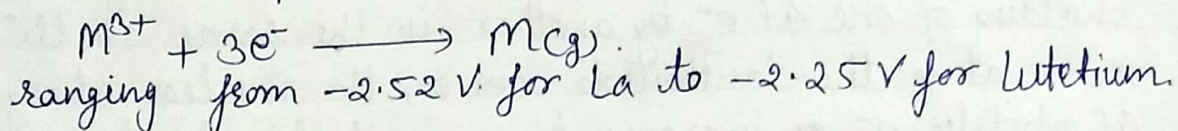
2. Cause of Lanthanide Contraction:- The cause of lanthanide contraction is generally to imperfect shielding of one $4f$ e^- by another in the same shell. Thus as we move along the lanthanide series, the nuclear charge & the no. of $4f$ orbital's e^- increase by one unit at each step. However due to imperfect shielding (because the shape of f orbitals is very much diffused) the net effective nuclear charge increases which causes contraction although small in the size of the e^- charge cloud & thus each ion shrinks in comparison with its predecessor.
e.g.:- in going from La^{3+} to Lu^{3+} the ionic radii decrease from 106 to 85 pm.

3. Consequence of Contraction:-

- (1) Electronegativity:- There is a slight increase in electronegativity of trivalent ions.
- (ii) Ionic Radius:- There is a steady decrease in the ionic size.
- (iii) Anomalous Behaviour of Post Lanthanide elements:- The elements which follow lanthanides are called post lanthanide elements. Thus these are the elements of third transition series. Lanthanide contraction effect is more pronounced in post lanthanide elements in atomic radii & etc.
- (iv) Basicity Difference:- There is a decrease in basic strength of the oxides & hydroxides of lanthanides & with increase in atomic no. Thus $La(OH)_3$ is the most basic while $Lu(OH)_3$ is the least basic.

Teacher's Signature : _____

(iv) E° Value:- There is a small but smooth increase in standard electrode potential values, E° for the process.



(v) Resemblance of II & IIIrd Transition Series:- we find that there is almost no change in ionic radius when we move from Zr. to Hf, Nb to Ta & Mo to W, etc. As the filling takes place in inner f-orbitals, the ionic radii of the above couples remains almost constant.

\Rightarrow Because of very small change in the ionic radius, the props. of lanthanide elements show similar properties. This creates problems in separation of lanthanide from one another.

4. Colors of Lanthanide Compounds:- The lanthanide metals are silvery white but the trivalent lanthanide ions show different colours. Color of ions depends on the no. of unpaired e^- because the elements with x f e^- often have a similar colour to those of $(14-x)$ f e^- . This is evident from table. The colour transmitted is the colour shown by the substance.

"Table:- for Colours"

no. of unpaired e^-	elements ions	Colour
0	$\text{La}^{3+}, \text{Lu}^{3+}$	Colourless
1	$\text{Ce}^{3+}, \text{Yb}^{3+}$	Colourless
2	$\text{Pr}^{3+}, \text{Tm}^{3+}$	Green
3	$\text{Nd}^{3+}, \text{Er}^{3+}$	Red
4	$\text{Pm}^{3+}, \text{Ho}^{3+}$	Pink & yellow respectively
5	$\text{Sm}^{3+}, \text{Dy}^{3+}$	Yellow.
6	$\text{Eu}^{3+}, \text{Tb}^{3+}$	Pink.
7	Gd^{3+}	Colourless.