Chemistry of Lanthanide Elements

The elements which have partly filled (n-2) f orbital are called f-block element.

These elements are also called inner transition element and divided into two series:

- **Lanthanide Series** — This series includes fourteen element from ~~Th~~ Ce$_{58}$ to Lu$_{71}$. In the elements of this series the additional electron goes to 4f-orbital.

- **Actinide series** — This series includes also fourteen elements from $_{90}$Th to $_{103}$Lw. In the element of this series the additional electron goes to 5f-orbital.

The inner transition of element are thoese element which possess both d and -f orbital respectively.

Lanthanide Shell —

The series include 14 element from Ce to Lu a group of 14 element in which additional electron goes to 4f - orbital are (n-2)th main shell are called lanthanide. These are also known as rare earth element because they are found

The name of 14 element of lanthanide series element are given below —

	Symbol	Name
सीने	58Ce	Cerium
पर	59Pr	Praseodymium
नदियाँ	60Nd	Neodymium
प्रेम की	61Pm	Promethium
समाधी	62Sm	Samarium
यूँ	63Eu	Europium
गवगद	64Gd	Gadolinium
तब	65Tb	Terbium
दिल	66Dy	Dysprosium
हुआ जुश	67Ho	Holmium
और	68Er	Erbium ~~Tm~~

क्रम 69 Tm Thulium

क्रम 70 Yb Ytterbium

लाल्टानम Lu Lutetium

General properties of lanthanide —

The general property of lanthanide series is similar to transition metal atom some property of lanthanide is given below —

Electronic configuration —

The electronic configuration of lanthanide series the energy of 5d and 4f orbital is near about similar and thus their filing of so certain irregularities. The electronic configuration of lanthanide in their ground state is given below:-

Trick —

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Electron in 4f	1		3	4	5	6	7	7	9	10	11	12	13	14

Element	Configuration	Oxidation states
58Ce सीट	$[Xe]\ 4f^{1}, 5d^{1}, 6s^{2}$	+3, +4
59Pr पर	$[Xe]\ 4f^{3}, 5d^{0}, 6s^{2}$	+3, +4
60Nd नहीं	$[Xe]\ 4f^{4}, 5d^{0}, 6s^{2}$	+2, +3, +4
61Pm पीटो	$[Xe]\ 4f^{5}, 5d^{0}, 6s^{2}$	+3
62Sm सुनो	$[Xe]\ 4f^{6}, 5d^{0}, 6s^{2}$	+2, +3
63Eu यूँ	$[Xe]\ 4f^{7}, 5d^{0}, 6s^{2}$	+2, +3
64Gd गुड़िया	$[Xe]\ 4f^{7}, 5d^{1}, 6s^{2}$	+3
65Tb टीवी	$[Xe]\ 4f^{9}, 5d^{0}, 6s^{2}$	+3, +4
66Dy दिखती	$[Xe]\ 4f^{10}, 5d^{0}, 6s^{2}$	+3, +4
67Ho हो	$[Xe]\ 4f^{11}, 5d^{0}, 6s^{2}$	+3
68Er इधर	$[Xe]\ 4f^{12}, 5d^{0}, 6s^{2}$	+3
69Tm तुम	$[Xe]\ 4f^{13}, 5d^{0}, 6s^{2}$	+2, +3
70Yb यो ग्री	$[Xe]\ 4f^{14}, 5d^{0}, 6s^{2}$	+2, +3
71Lu लो	$[Xe]\ 4f^{14}, 5d^{1}, 6s^{2}$	+3

Oxidation number—

Most of the common oxidation number is +3 all lanthanide series but it can show +2, +4 oxidation state when they accchive stable configuration f^0, f^7, f^{14}. There are some element which is show +2, +4 oxidation state these are given below—

Magnetic properties—

Most of the lanthanide series element are show paramagnetic property due to presence of unpaired electron and some element of diamagnetic due to presence of paired electron.

Paramagnetic substance are attracted in magnetic field but diamagnetic

In general the magnetic property of these element determined by magnetic movement

The magnetic movement arise from two type motion of electron.
The magnetic movement arise from two type —

(i) spin motion
(ii) Orbital motion

The spin motion of electron produces spin magnetic moment while the orbital motion of electron produces orbital magnetic moment.

The magnetic property of the lanthanides are different from those of the transition elements. For f-block element, the electric field of ligands does not restricted the orbital motion of electron thus, orbital moment which was ignored in d-block but can not ignored in case of f-block element.

The magnetic moment in such case can be calculated by the following formula —

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

where, 'g' is lande splitting factor

and 'J' is the total angular momentum.

Formation of complex compound

Most of lanthanide element show +3 oxidation state. Its f- and d- orbital are incomplete. It is completed by gaining/accepting pair of electron to form complex compound.

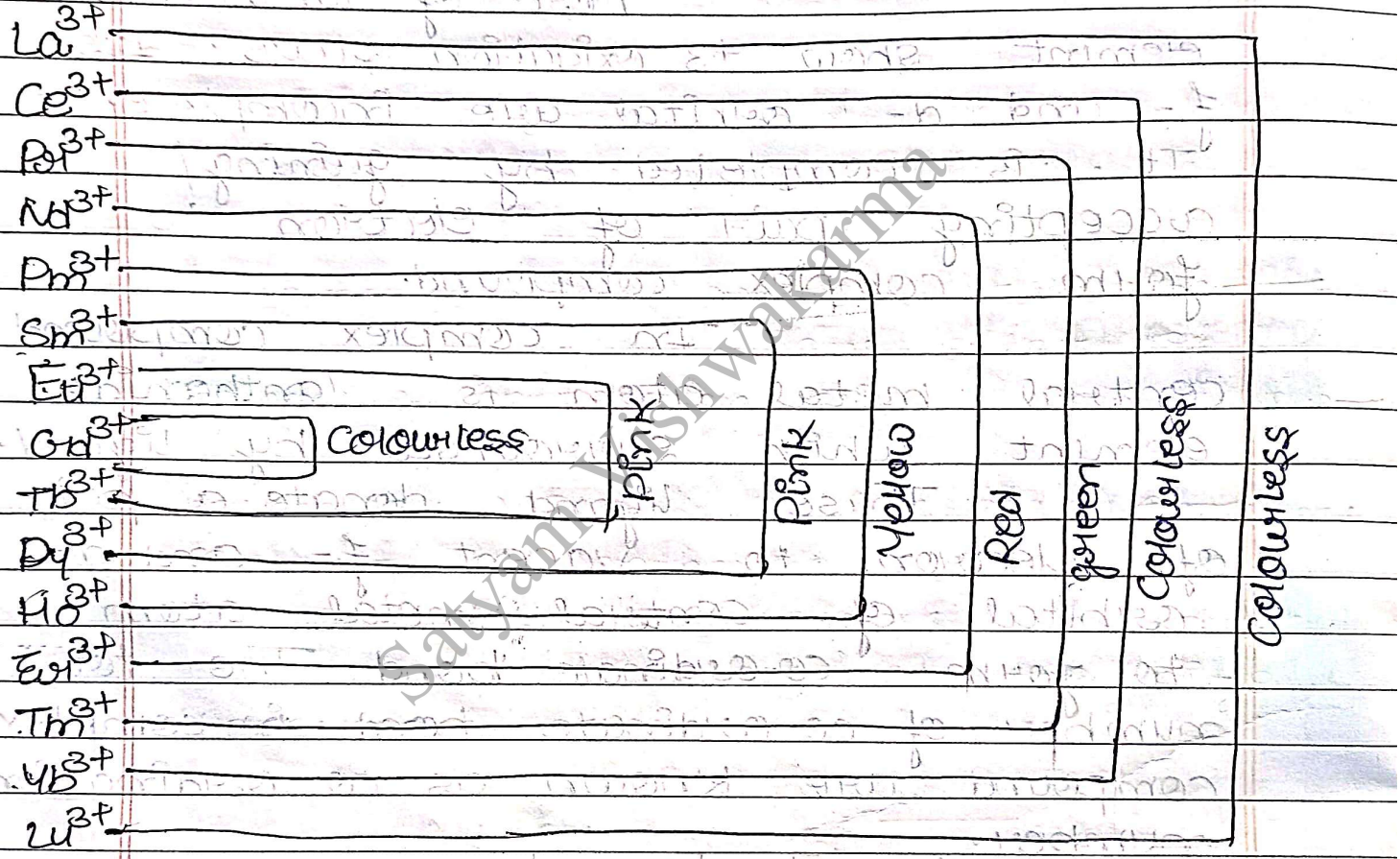
In complex compound central metal atom is lanthanide element which surrounded by ligand. These ligand donate a pair of electron to vacent f- and d- orbital of central metal atom to form co-ordinate bond. The total number of co-ordinate bond in complex compound are known as co-ordination number.

eg- $[ML_2]$ $[ML_3]$

lanthenide element have less tendency to complex formation due to high charge and large size.

Colour property—

Some trivalent ion of lanthanide series are coloured in solid and liquid state.



Ionic and atomic radii — (lanthanide contraction) —

In lanthanide series their is a regular decrease in the atomic size as well as atomic radii of trivalent ion as the

atomic number increase this decrease in size of atom is known as lanthanide contraction. Atomic radii do show some irregularities but ionic radii are decreases from La to Lu.

Atoms	atomic size	ionic size
Ce	183	103
Pr	182	101
Nd	181	99
Pm	181	98
Sm	180	96
Gd Eu	180	95
Gd	1980	94
Tb	178	92
Dy	177	91
Ho	176	89
Er	175	88
Tm	174	87
Yb	173	86
Lu	170	86

On the moving from Ce to Lu decrease in atomic radii from 183 to 170 i.e. the decrease in only 13 pm similarly the decrease ionic radii 103 - 86 pm i.e. decrease only 17 pm. cause of

Cause of lanthanide contraction—

The size of lanthanide series are decreases with increase atomic number because the number of nuclear charge outer most shell electron increases with increase an atomic number.

Effect of lanthanide contraction—

Some effect of lanthanide contraction are given below—

I] hardness (MP and BP increase) of some element of lanthanide series are higher this is becomes the attraction between the atom as the size decreases.

II] Similarties of chemical property—

The change in the ionic radii in lanthanide series is very small. Therefore, chemical property of these element are simlar. Thus, it is very difficult to separate these element in pure state.

Basic strength of hydroxides

The size of lanthanide series is decreases therefore the basic strength of OH^- is decreases because OH^- group is strongly attached to inner transition metal ion so, OH^- ion is not easily remove therefore $[Ce(OH)_3]$ is more basic than $[Lu(OH)_3]$

Q- $[La(OH)_3]$ is more basic than $[Lu(OH)_3]$ why?

Ans- $La(OH)_3$ is more basic than $Lu(OH)_3$ because when we move from in lanthanide series then the size of these element generally decrease therefore the size of La is larger than Lu and La is loosely bonded with OH^- and easily remove OH^- so it is more basic.

Due to smaller size of Lu it is tightly bonded to OH^- hence it is not easily remove OH^- so it is less basic.

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Chemistry of Actinides

A group of 14 element in which the additional e⁻ goes to 5f orbital of (n-2) main shell are called actinide or actinones or 5f-block element. The elements beyond 'U' which does not occurs in nature. The elements having atomic number higher than 'U' are known as trans-uranic element. These element are man-made. The 14 elements of actinide are —

$_{89}Ac$ $_{90}Th$ $_{91}Pa$ $_{92}U$ $_{93}Np$ $_{94}Pu$ $_{95}Am$ $_{96}Cm$ $_{97}Bk$
इसे थोरस पाकरी यूरेप नापने पहुँचे अमेरिका कमिंग बैंक of
$_{98}Cf$ $_{99}Es$ $_{100}Fm$ $_{101}Md$ $_{102}No$ $_{103}Lw$
कैलिफोर्निया स्टेट फेमस मैडम नोआ के लेकर आये

Properties of actinides —

Electronic configuration —

The electronic configuration of outermost shell of these element are given below—

Trick-	1	2	3	4	5	6	7	8	9	10	11	12	13	14
einsf-	1	2	3	4	5	7	7	9	10	11	12	13	14	14

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~~89 Ac~~

Element	E. Configuration	Oxidation No.
90 Th (थोरियम)	$[Rn]\ 5f^0, 6d^2, 7s^2$	+3, +4
91 Pa (पादरी)	$[Rn]\ 5f^2, 6d^1, 7s^2$	+3, +4, +5
92 U (यूरेप)	$[Rn]\ 5f^3, 6d^1, 7s^2$	+3, +4, +5, +6
93 Np (नाचने)	$[Rn]\ 5f^4, 6d^1, 7s^2$	+3, +4, +5, +6, +7
94 Pu (पहुँचे)	$[Rn]\ 5f^5, 6d^1, 7s^2$	+2, +3, +4, +5, +6
95 Am (अमेरिका)	$[Rn]\ 5f^7, 6d^0, 7s^2$	+3, +4
96 Cm (कमिंग)	$[Rn]\ 5f^7, 6d^1, 7s^2$	+3, +4
97 BK (बैंक of)	$[Rn]\ 5f^9, 6d^0, 7s^2$	+2, +3
98 Cf (कैलिफोर्निया)	$[Rn]\ 5f^{10}, 6d^0, 7s^2$	+2, +3
99 Es (स्टेट)	$[Rn]\ 5f^{11}, 6d^0, 7s^2$	+2, +3
100 Fm (फेमस)	$[Rn]\ 5f^{12}, 6d^0, 7s^2$	+2, +3
101 Md (मैडम)	$[Rn]\ 5f^{13}, 6d^0, 7s^2$	+2, +3
102 No (नोआ को)	$[Rn]\ 5f^{14}, 6d^0, 7s^2$	+2, +3
103 Lw (लेकर आये)	$[Rn]\ 5f^{14}, 6d^1, 7s^2$	+3

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Oxidation state—

Most of the actinides series element shows +3 oxidation number but some element shows +2 to +7 the different oxidation state. The +4 state is shown of first 6 element and +5 oxidation state shown by five element and +7 oxidation state is shown by Pu and Np. In oxidation variation is because on the element of actinide, The energy of 5f, 6d and 7s near about similar.

Magnetic property—

Most of the ion of actinide series are paramagnetic i.e. they are attached in magnetic field. This is due to the presence of unpaired electron Ac^{++}, Th^{4+}, Lw^{3+} are diamagnetic which are repulled in magnetic field. The magnetic properties of these element can be explain on the basis of magnetic moment. The magnetic moment of these can be calculated by the following formula—

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

OR

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

Actinide contraction

The atomic and ionic radii decreases with increasing of atomic number when we move actinide series from left to right. It has been observed that on going Ac^{+++} to Cm^{+++}, Ionic radii decreases from 99A° – 88A°. This regular decrease the atomic and ionic radii in actinide element are known as actinide contraction.

The contraction is causes due to increasing the number of nuclear charge the attraction between outer most shell electron and nuclear charge increasing show, the size of atom or ion decreases

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Similarities of Lanthenide and actinide series ——

There are some similarities between lanthenide and actinide series —

i- both the series there is irregular filling of f-orbital in their electronic configuration.

ii- Both shows common oxidation number +3.

iii- Both are electropositive and high chemical reactivity.

iv- There is a decrease in the atomic/ionic size in both the series with increase in atomic number.

v- The elements of both series are paramagnetic

vi- Both have tendency to form complex compound.

Difference between lanthenide and actinide ——

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	Lanthenide	Actinide
i-	The electrons enters in 4f-orbital	i- The electron enters in 5f-orbital
ii-	Their highest oxidation state is +4.	ii- They show highest oxidation state +6, +7
iii-	Their paramagnetic property easily explained	iii- They are also paramagnetic but it is difficult to explain their magnetic property
iv-	4f-electron have greater shielding effect	iv- It have less shielding effect
v-	They have less tendency to formation of complex	v- They have greater tendency to form complex compound.
vi-	They are non-radio-active	vi- They are radio-active

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Oxidation and Reduction

Oxidation number ——

Oxidation number of atom is the charge on the atom in compound.

general rule to calculate the oxidation number ——

The following rule to determine the oxidation number of the element.

i- Oxidation number of an element in the combined or free state is zero

ii- Oxidation number of hydrogen in all its compound is +1. but in hydride the oxidation number of hydrogen is −1

iii- Oxidation number of oxygen in all its compound is −2 but in peroxide in −1 and OF_2 in +2.

iv- Oxidation number of alkali metal is +1 and alkali earth metal have +2.

v- The oxidation number of ion or radical is equal to the charge present in it.

vi- The sum of oxidation number of all the atom in a given molecule is zero. and is determined by the sum of oxidation number of the individual atom each multiplied by number of atom present in molecule

vii- The sum of the oxidation number of the atom in a poly atomic ion is equal to the charge carried by the ion.

Older concept of oxidation and Reduction—

According to this concept The addition of oxygen or removed of hydrogen is called oxidation and addition of hydrogen or removed of oxygen is called reduction.

$H_2S + Cl_2 \rightarrow S + 2HCl$ (oxidation)

$Fe_2O_3 + CO \longrightarrow Fe + 3CO_2$ (Reduction)

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Diffination based on the electron transfer. (Electronic concept) →

According to this concept oxidation is a process in which ion, atom or molecule losses one or more electron. On the other hand, reduction is a process in which an ion, atom or molecule accept one or more electron.

Example-

$Na \rightarrow Na^{+} + e^{-}$ oxidation

$H_2 \rightarrow 2H^{+} + 2e^{-}$ oxidation

$Sn^{4+} + 2e^{-} \rightarrow Sn^{2+}$ Reduction

$MnO_4^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_2O$ Reduction

Difination based on oxidation number —

According to this concept oxidation can be defind as a process in which oxidation number of effective element increases and reduction is a process in which oxidation number of effective element decreases.

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$H_2\overset{-1}{O}_2 \longrightarrow O_2 + 2H^+$ (oxidation)

$[Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{4-}$

Redox reaction —

A reaction in which oxidation and reduction takes place simultaneously is called Redox or oxidation- Reduction reaction.

$$\overset{+2}{Sn}Cl_2 + 2\overset{+2}{Hg}Cl_2 \longrightarrow \overset{+4}{Hg_2}Cl_2 + \overset{+4}{Sn}Cl_4$$

(Reduction: $+2 \rightarrow +1$; Oxidation: $+2 \rightarrow +4$)

Oxidasing agent —

An oxidasing agent have some properties—

i- It oxidasied some other substance and itself it reduced.

ii- It losses oxygen or any electro-negative element.

iii- It accept Hydrogen or any electro-positive element.

iv- It gains one or more electron.

v- Oxidation number of effective element decreases.

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Reducing agent —

Reducing agent have some properties —

i- It reduced some other substance and itself it oxidasied.

ii- It losses Hydrogen or any electro positive element.

iii- It accept oxygen or any electro negative element.

iv- It losses one or more electron.

v- Oxidation number of effective element increases.