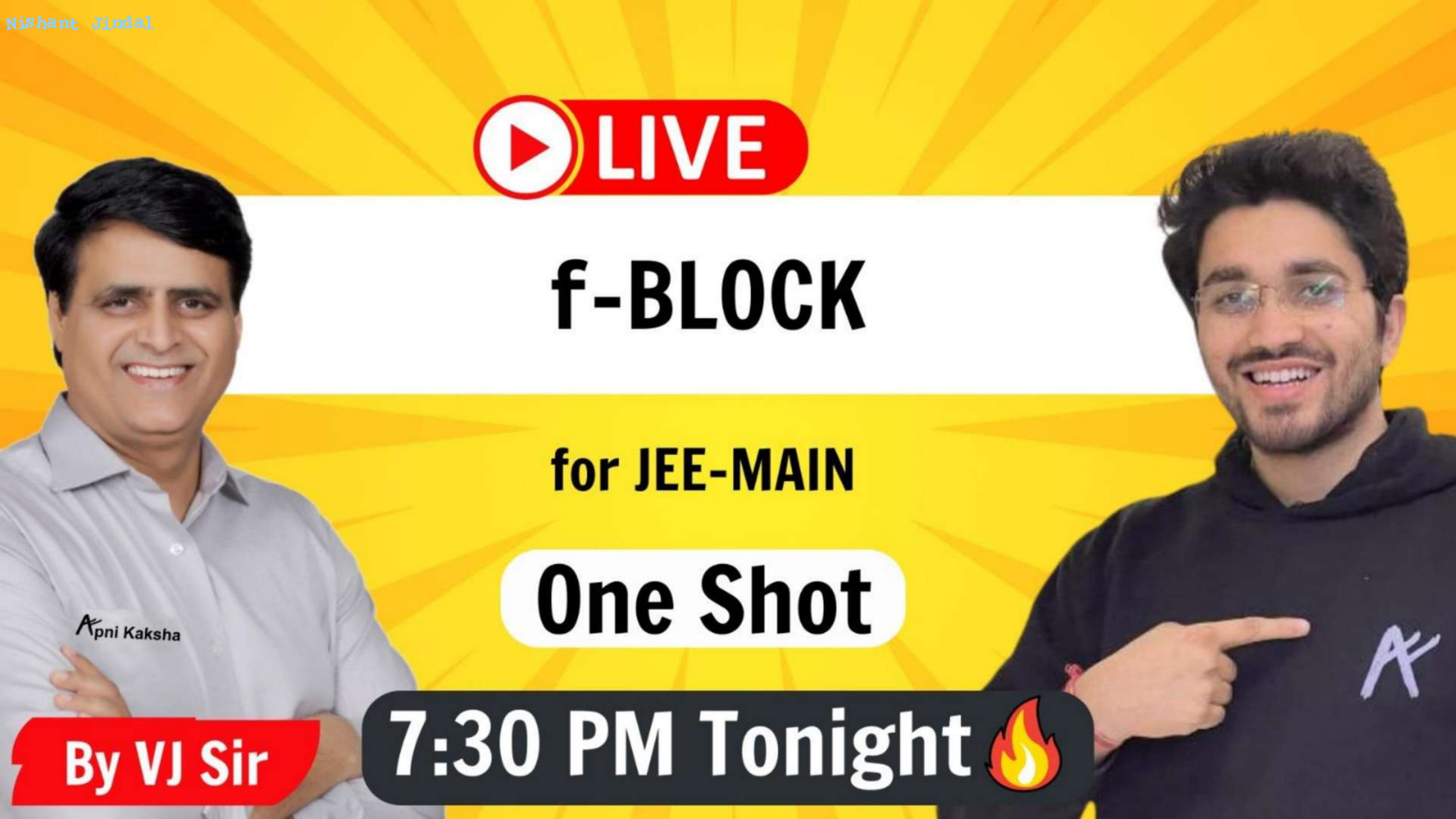

LIVE
f-BLOCK
for JEE-MAIN
One Shot
Apni Kaksha
By VJ Sir
7:30 PM Tonight

f - Block

Inner Transition Elements:

The elements in which the additional electron enters in (n-2)f orbitals are called inner transition elements or f-block elements.

Position in the periodic table:

The lanthanides resemble with Yttrium in most of their properties. So it became necessary to accommodate all the fifteen elements together at one place. This has been done by placing the first element, lanthanum below yttrium and placing the remaining fourteen elements separately in the lower part of the periodic table.

Lanthanide series (Z= 58 -71) (Ce - Lu) — 4f series

Actinide series (Z = 90 - 103) (Th - Lr) — 5f series

Nishant Jindal

IIIB | 3^{rd}

3d series	I	$_{21}Sc$	Ti - - - -	Zn	4^{th}
4d series	II	$_{39}Y$	Zr - - -	Cd	5^{th}
5d series	III	$_{57}La$	Hf - - -	Hg	6^{th}
		$_{89}Ac$	Ku/Rf - - -		7^{th}

$_{58}Ce \longrightarrow {}_{71}Lu$ — 4f series | Lanthanide — 6^{th}

$_{90}Th \longrightarrow {}_{103}Lr$ — 5f series | Actinide — 7^{th}

Position

f - Block

LANTHANIDES (RARE EARTHS OR LANTHANONES)

(i) Lanthanides are reactive elements so do not found in free state in nature.

(ii) Most important minerals for lighter Lanthanides are - Monazite, cerites and for heavier lanthanides -Gadolinite and Xenotime

Electronic configuration:

(i) The general configuration of lanthanides may be given as $4f^{1-14}5s^25p^65d^{0-1}6s^2$.

6s

4f

(n-2)

n=6

Nishant Jindal

f - Block

Imp.

tripositive ion

Atomic Number	Element	Symbol	Outer electronic configuration	
			Atomic	+3 ion
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^1$
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^2$
60	Neodymium	Nd	$4f^4 6s^2$	$4f^3$
61	Promethium	Pm	$4f^5 6s^2$	$4f^4$
62	Samarium	Sm	$4f^6 6s^2$	$4f^5$
63	Europium	Eu	$4f^7 6s^2$	$4f^6$
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7$
65	Terbium	Tb	$4f^9 6s^2$	$4f^8$
66	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^9$
67	Holmium	Ho	$4f^{11} 6s^2$	$4f^{10}$
68	Erbium	Er	$4f^{12} 6s^2$	$4f^{11}$
69	Thulium	Tm	$4f^{13} 6s^2$	$4f^{12}$
70	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{13}$
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14}$

Ce सिर = $4f^1 5d^1 6s^2$

Pr पर लेकर = $4f^3 6s^2$

Nd नौ दिये = $4f^4 6s^2$

Pm परमेश्वरी = $4f^5 6s^2$

Sm समझाये = $4f^6 6s^2$

Eu रो = $4f^7 6s^2$

Gd गए $4f^7 5d^1 6s^2$ [Half filled]

Tb तब = $4f^9 6s^2$

Dy दियो = $4f^{10} 6s^2$

Ho हो = $4f^{11} 6s^2$

Er इर = $4f^{12} 6s^2$

Tm तुम = $4f^{13} 6s^2$

Yb इब = $4f^{14} 6s^2$

Lu लुटने आये $4f^{14} 5d^1 6s^2$

Nishant Jindal

Keypoint ⇒ Lanthanide ⇒ +3 [stable]

~~ne~~ $Ce(SO_4)_2$ is good a good oxidising agent

+4 → +3 ← +2

(O.A) (R.A)

* Ce^{+4} because of Noble gas conf.

$Ce^{+4} < Ce^{+3}$

$Ce^{+4}/Ce^{+3} = +1.74$ ev/atom

$\boxed{\Delta G = -nFE^{\circ}}$

it oxidise → water also and use as a quilatative analysis

Nishant Jindal

$$\underbrace{\left.\begin{array}{l} Eu^{+2} = 4f^{7} \text{ — Half filled} \\ Yb^{+2} = 4f^{14} \text{ — fully filled} \end{array}\right\}}_{R\cdot A}$$

Tb^{+4} — $4f^{7}$ Half filled

(O·A)

f - Block

(ii) It is to be noted that filling of $4f$ orbitals in the atoms is not regular. A $5\ d$ electron in gadolinium $(Z = 64)$ with an outer electronic configuration of $4f^7 5d^1 6s^2$ (and not $4f^8 6s^2$). This is because the $4f$ and $5\ d$ electrons are at about the same potential energy and that the atoms have a tendency to retain stable half filled configuration.

(iii) On the other hand, the filling of f-orbitals is regular in tri-positive ions.

(iv) After losing outer electrons, the f-orbitals shrink in size and became more stable.

(v) Pm is the only synthetic radioactive lanthanide.

Lanthanide are Non Radioactive except Pm

f - Block

(iii) The cumulative effect of the contraction of the lanthanoid series, known as lanthanoid contraction, causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr(160 pm) and Hf(159pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

GENERAL CHARACTERISTICS :

Sm

(i) All the lanthanoids are silvery white soft metals and tarnish rapidly in air.

(ii) The hardness increases with increasing atomic number, samarium being steel hard.

(iii) Their melting points range between 1000 to 1200" " K but samarium melts at 1623 K.

f - Block

(iv) They have typical metallic structure and are good conductors of heat and electricity.

(v) Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.

(vi) Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of f electrons. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so. However, absorption bands are narrow, probably because of the excitation within f level.

(vii) The lanthanoid ions other than the f^0 type $\left(La^{3+}\right.$ and $\left.Ce^{4+}\right)$ and the f^{14} type $\left(Yb^{2+}\right.$ and $\left.Lu^{3+}\right)$ are all paramagnetic.

Nishant Jindal

f - Block

(viii) The first ionisation enthalpies of the lanthanoids are around 600 kJ mol-1, the second about 1200 kJ mol-1 comparable with those of calcium. A detailed discussion of the variation of the third ionization enthalpies indicates that the exchange enthalpy considerations (as in 3 d orbitals of the first transition series), appear to impart a certain degree of stability to empty, half-filled and completely filled orbitals f level. This is indicated from the abnormally low value of the third ionisation enthalpy of lanthanum, gadolinium and lutetium.

600 1200

IIA

f - Block

(Oxidation states in brackets are unstable states)

(i) The lanthanides contains two s electrons in the outermost shell, they are therefore expected to exhibit a characteristic oxidation state of +2 . But for the lanthanides, the +3 oxidation is common.

(ii) This corresponds to the use of two outermost electrons $(6\ s^2)$ alongwith one inner electron. The inner electron used is a $5\ d$ electron (in La, Gd and Lu), or one of the $4f$ electron if no $5\ d$ electrons present.

(iii) All the lanthanides attains +3 oxidation state and only Cerium, Praseodymium, and Terbium exhibit higher oxidation state (+4). Eu and Yb exhibit +2 oxidation state.

f - Block

(iv) Oxidation states +2 and +4 occur particularly when they lead to -

(a) A noble gas configuration Ex. $Ce^{4+}(f^0)$

(b) A half filled 'f' orbital Ex. Eu^{2+}, Tb^{4+}, (f^7)

(c) A completely filled ' f ' orbital Ex. $Yb^{2+}(f^{14})$

(v) Therefore, in higher oxidation state, they act as oxidising while in lower state as reducing agents.

Magnetic properties:

(i) In tripositive lanthanide ions the number of unpaired electrons regularly increases from lanthanum to Gadolinium (0 to 7) and then continuously decreases upto lutecium (7 to 0).

(ii) lanthanum and lutecium ions are diamagnetic, while all other tripositive lanthanide ions are paramagnetic. (Exception - Neodyomium is the most paramagnetic lanthanide).

f - Block

(iii) Ce^{+4} and Yb^{+2} are also diamagnetic ions.

$4f^1$ to $4f^{13}$ col.
$4f^0$ $4f^{14}$ — col. less
$4f^n$ and $4f^{14-n}$ same col.

Colour:

(i) The lanthanide ions have unpaired electrons in their $4f$ orbitals. Thus these ions absorbs visible region of light and undergo $f - f$ transition and hence exhibit colour.

(ii) The colour exhibited depends on the number of unpaired electrons in the $4f$ orbitals.

(iii) The ions often with $4f^n$ configuration have similar colour to those ions having $4f^{14-n}$ configuration.

(iv) Lanthanide ions having $4f^0$, $4f^{14}$ are colourless.

Other Properties:

Highly dense metals with high m.pts. do not show any regular trend.

f - Block

Charge density | +ive charge ↑ acidic ch ↑

Ionisation Energies: Lanthanides have fairly low ionisation energies comparable to alkaline earth metals.

$M \longrightarrow M^+$

(R.A)

Electro positive character: $\boxed{\text{High due to low I.P.}}$

Complex formation: Do not have much tendency to form complexes due to low charge density because of their large size. Lu^{+3} is smallest in size can only form complex.

Reducing Agent: They readily lose electrons so are good reducing agent.

Alloy: Alloys of lanthanides with Fe are called mish metals.

95% Ln + 5% Fe Ca|Al|C|S traces

A well known alloy is mischmetall which consists of a lanthanoid metal (95%) and iron $(\sim 5\%)$ and traces of S, C, Ca and Al.

Ce

Lu

Basic Nature: $La(OH)_3$ is most basic in nature while $Lu(OH)_3$ least basic.

Carbide: Lanthanides form MC_2 type carbide with carbon, which on hydrolysis gives C_2H_2.

CHEMICAL PROPERTIES:

$X + H^{+}-Cl^{-} \longrightarrow H_2$

(i) In their chemical behaviour, in general, the earlier members of the series are quite reactive similar to calcium but, with increasing atomic number, they behave more like aluminium. Values for $E^{\ominus}$ for the half-reaction :

$Ln^{3+}(aq) + 3e \rightarrow Ln(s)$

are in the range of -2.2 to $-2.4\ V$ except for Eu for which the value is $-2.0\ V$. This is, of course, a small variation.

(ii) The metals combine with hydrogen when gently heated in the gas.

(iii) The carbides, Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon.

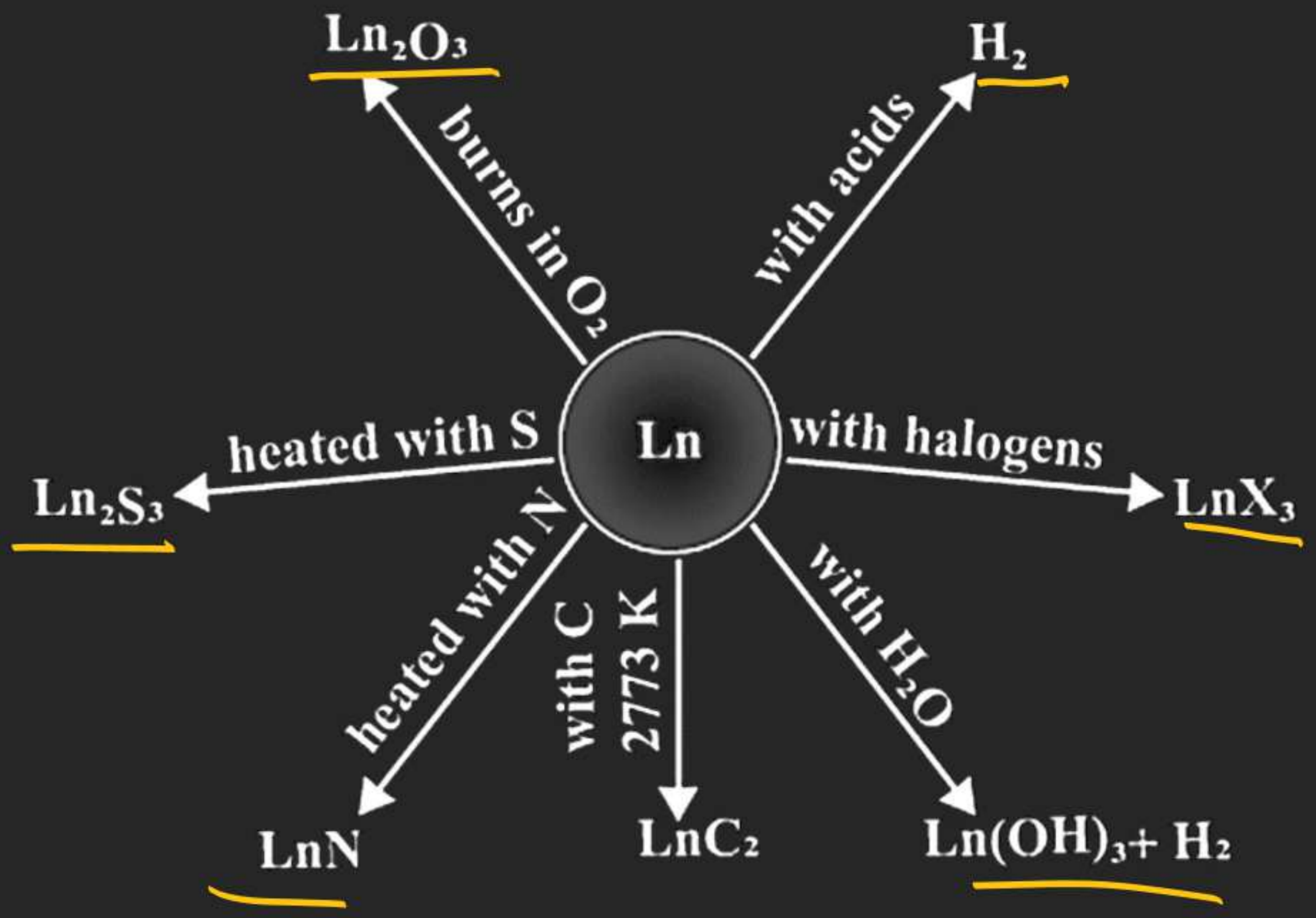
(iv) They liberate hydrogen from dilute acids and burn in halogens to form halides.

(v) They form oxides M_2O_3 and hydroxides $M(OH)_3$. The hydroxides are definite compounds, not just hydrated oxides.

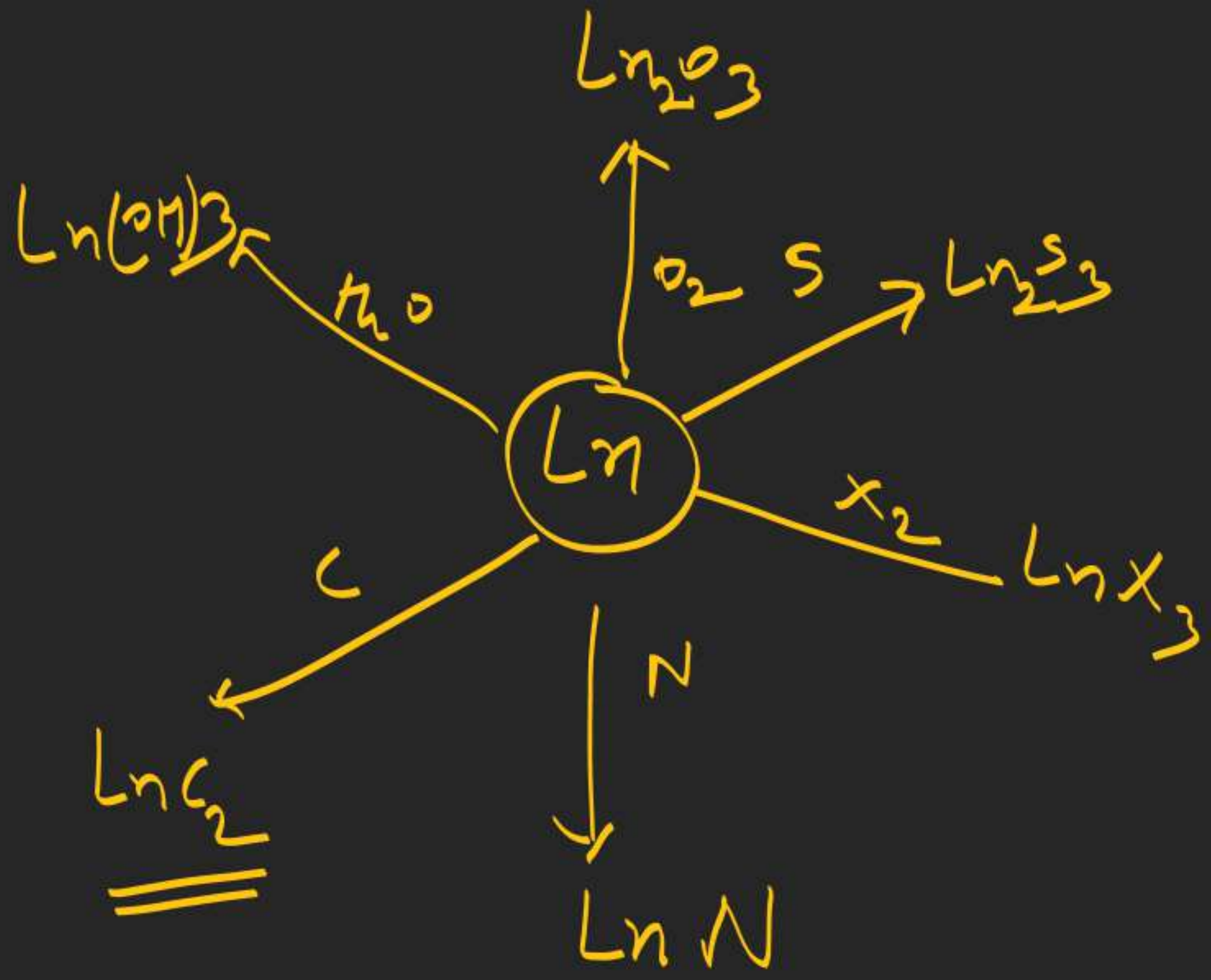
(vi) They are basic like alkaline earth metal oxides and hydroxides.

(vii) Their general reactions are depicted in Fig.

f - Block



Chemical reactions of the lanthanoids



<u>alloy</u>

misch metal

95% Lanthanide + 5% Fe and small amount traces S | Al | Ca | C

$Ti < Zr \approx Hf$

160pm 159pm

Sc	Ti
Y	Zr
57 La	Hf 72
89 Ac	Ku/Rf 104

$Ti < Zr$

S.E

$s > p > d > f$

$\underset{58}{Ce} \longrightarrow \underset{71}{Lu} = 4f$ series

$\underset{90}{Th} \longrightarrow \underset{103}{Lr} = 5f$ series

4f 5d 6s6p

f - Block

Application of lanthanides:

Cerium is most useful element in the lanthanides -

- Ceramic application $-CeO_2, La_2O_3, Nd_2O_3$ and Pr_2O_3 are used as decolourizing agents for glasses.
- CeS (m.p. $-2000°C$) is used in the manufacture of a speciel type of crucibles and refractories.
- Lanthanide compounds like cerium molybdate, cerium tungstate are used as paints and dyes.
- In textile and leather industries (Ce salts).
- Mish metal is pyropheric and is used in cigarette & gas lighter.
- The best single use of the lanthanoids is for the production of alloy steels for plates and pipes.
- A good deal of mischmetall is used in Mg-based alloy to produce bullets, shell and lighter flint.

f - Block

- Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking.
- Some individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

DO YOUR SELF – 1

1. Last element of lanthanide series is -

(A) Lawrencium (B) Lutetium

(C) Thulium (D) Hafnium

2. Which of the following statement is not correct?

(A) $La(OH)_3$, is less basic than $Lu(OH)_3$

(B) In lanthanide series, ionic radius of Ln^{3+} ions decreases

(C) La is actually an element of transition series rather than lanthanide series

(D) Atomic radii of Zr and Hf are same because of lanthanide contraction.

f - Block

ACTINIDES (f - BLOCK ELEMENTS)

(i) The elements in which the extra electron enters 5 f-orbitals of $(n-2)$ th main shell are known as actinides.

(ii) The man-made eleven elements $\boxed{Np_{93} - Lr_{103}}$ are placed beyond uranium in the periodic table and are collectively called trans-uranium elements.

(iii) Th, Pa and U first three actinides are natural elements.

Electronic configuration:

The general configuration of actinides may be given as $5f^{1-14} 6\ d^{0-1}, 7\ s^2$.

$\left.\begin{array}{l} _{90}Th \\ _{91}Pa \\ _{92}U \end{array}\right\}$ natural Radio

Nishant Jindal

f - Block

Ac से

Atomic No.	Elements	Symbol	Electronic Configuration
90	Thorium	Th था	$5f^0 6d^2 7s^2$
91	Proactenium	Pa पा	$5f^2 6d^1 7s^2$
92	Uranium	U यू	$5f^3 6d^1 7s^2$
93	Neptunium	Np नेपाली	$5f^4 6d^1 7s^2$
94	Plutonium	Pu पुरे	$5f^6 6d^0 7s^2$
95	Americium	Am अमेरिकन	$5f^7 6d^0 7s^2$
96	Curium	Cm सेमिलते	$5f^7 6d^1 7s^2$
97	Berkellium	Bk बेक	$5f^9 6d^0 7s^2$
98	Californium	Cf फ्रफ	$5f^{10} 6d^0 7s^2$
99	Einstenium	Es ऐसा	$5f^{11} 6d^0 7s^2$
100	Fermium	Fm फिल्मी	$5f^{12} 6d^0 7s^2$
101	Mandelevium	Md मूड	$5f^{13} 6d^0 7s^2$
102	Nobellium	No ना	$5f^{14} 6d^0 7s^2$
103	Lowrencium	Lr लोजो	$5f^{14} 6d^1 7s^2$

f - Block

Oxidation states:

(i) In lanthanides and actinides +3 oxidation is the most common for both of the series of elements.

(ii) This oxidation state becomes increasingly more stable as the atomic number increases in the actinide series.

pyqs

(iii) Highest oxidation states in the actinides is +7 exhibited by Np_{93} & Pu_{94}, it is unstable.

(iv) Highest stable oxidation state is +6 shown by U_{92}.

Other Properties:

- Physical appearance: Acitinides are silvery white metals. They get tarnished when exposed to the attack of alkalies.
- Density: All the actinides except thorium and americium have high densities.

f - Block

- Colour: Actinide ions are generally coloured. The colour of actinide ions depends upon the number of 5f-electrons. The ions containing no unpaired 5f-electrons (exactly full filled $\mathrm{f}-$ subshell) are colourless, as expected.
- Ionisation energies: Ionisation energies values of actinides are low.
- Electropositive character: All the known actinide metals are highly electropositive. They resemble lanthanide series in this respect.
- Melting Boiling properties: They have high melting and boiling points. They do not follow regular gradation of melting or boiling points with increase in atomic number.
- Magnetic properties: The actinide elements are paramagnetic due to the presence of unpaired electrons.
- Radioactive nature: All the actinides are radioactive in nature.

Actinide contraction: The size of atom/cation decrease regularly along the actinides series. The steady decrease in ionic radii with increase in atomic number is referred to as actinide contraction. This is due to poor shielding of 5f-electrons

Comparison of lanthanides and Actinides

Points of Resemblance:

(i) Both lanthanides and actinides show a dominant oxidation state of +3 .

(ii) Both are electropositive and act as strong reducing agents.

(iii) Cations with unpaired electrons in both of them are paramagnetic.

(iv) Most of the cations of lanthanides and actinides are coloured.

(v) Both of them show a steady decrease in their ionic radii along the series. Thus, lanthanides show lanthanide contraction and actinides show actinide contraction.

Scandide < lanthanide < actinide

Nishant Jindal

f - Block

Difference between lanthanides & Actinides:

	Lanthanides		Actinides
1.	Besides the most common oxidation state of +3 lanthanides show +2 and +4 oxidation states in case of certain elements.	1.	Besides the most common state of +3, actinides show +4, +5 and +6 oxidation states in case of certain elements.
2.	Lanthanides have less tendency towards complex formation.	2.	Actinides have a stronger tendency towards complex formation.
3.	Except promethium, they are non-radioactive. Pm	3.	All the actinides are radioactive.
4.	Oxides and hydroxide of lanthanides are less basic.	4.	Oxides and hydroxides of actinides are more basic.

Some important uses of actinides are as follows -

Thorium: Thorium is used in atomic reactors as fuel rods and in the treatment of cancer.

Uranium: Uranium is used as nuclear fuel. Its salts are used in glass industry (for imparting green colour). textile industry and also in medicines.

Plutonium: Plutonium is used as fuel for atomic reactors as well as in atomic bombs.

f - Block

PYQS

1. The lanthanide ion that would show colour is :

(A) Gd^{3+} (B) Sm^{3+} (C) La^{3+} (D) Lu^{3+}

$Sm^{+3} = 4f^6 4s^2$

$Sm^{+3} = 4f^5$

f - Block

2. The maximum number of possible oxidation states of actinoides are shown by:

(A) Nobelium (No) and lawrencium (Lr)

(B) Actinium (Ac) and thorium (Th)

(C) Berkelium (Bk) and californium (Cf)

(D) Neptunium (Np) and plutonium (Pu)

highest o.s +7 Np Pu

Stable oxidate state = +6 U

f - Block

3. The effect of lanthanoid contraction in the lanthanoid series of elements by and large means:

(A) increase in both atomic and ionic radii

(B) decrease in atomic radii and increase in ionic radii

(C) decrease in both atomic and ionic radii

(D) increase in atomic radii and decrease in ionic radii

4. The lanthanoid that does NOT show +4 oxidation state is

(A) Tb (B) Dy (C) Ce (D) Eu

Eu^{+2}

f - Block

5. Mischmetal is an alloy consisting mainly of

(A) lanthanoid and actinoid metals

(B) actinoid and transition metals

(C) lanthanoid metals

(D) actinoid metals

Misch metal ⇒ Lanthanide = 95% + 5% Fe + Ca | Al | S | C

f - Block

6. The electronic configurations of bivalent europium and trivalent cerium are :

(atomic number : $Xe = 54, Ce = 58, Eu = 63$)

(A) $[Xe]4f^7, [Xe]4f^1$

(B) $[Xe]4f^7 6s^2, [Xe]4f^1$

(C) $[Xe]4f^7 6s^2, [Xe]4f^1 5d^1 6s^2$

(D) $[Xe]4f^7, [Xe]4f^1 5d^1 6s^2$

$Eu = 4f^7$

$Ce = \underline{4f^1 5d^1 6s^2}$

$\underline{Ce^{+3} = 4f^1}$

f - Block

7. The Eu^{2+} ion is a strong reducing agent in spite of its ground state electronic configuration (outermost):

[Atomic number of $Eu = 63$]

(A) $4f^7 6s^2$ (B) $4f^6$ (C) $4f^7$ (D) $4f^6 6s^2$

$Eu^{+2} = 4f^7$ Half filled

f - Block

8. The number of f electrons in the ground state electronic configuration of $\boxed{Np}$ (Z=93) is (Nearest integer)

$14 + 4 = \underline{18}$

Ac

Th

Pa

U

$_{93}Np = \underline{4f^{14}}$ $\underline{5f^{4}}$

f - Block

9. The number of $4f$ electrons in the ground state electronic configuration of Gd^{2+} is [Atomic number of $Gd = 64$]

(7)

$_{64}Gd = 4f^7 5d^1 6s^2$

f - Block

10. Number of electrons present in $4f$ orbital of Ho^{3+} ion is (Given Atomic No. of $Ho = 67$)

10

$Ho = 4f^{11}\ 6s^{2}$

$Ho^{+3} = 4f^{10}$

f - Block

11. Given below are two statement: one is labelled as Assertion A and the other is labelled as Reason R:

Assertion A: Size of Bk^{3+} ion is less than Np^{3+} ion. Reason R : The above is a consequence of the ~~lanthanoid~~ contraction. In the light of the above statements, choose the correct answer from the options given below :

(A) A is false but R is true

(B) Both A and R are true but R is not the correct explanation of A

(C) Both A and R are true and R is the correct explanation of A

(D) A is true but R is false

Actinide contraction

f - Block

12. Given below are two statements:

Statement I : The E° value of Ce^{4+}/Ce^{3+} is $+1.74\ V$

Statement II : Ce is more stable in Ce^{4+} state than Ce^{3+} state.

In the light of the above statements, choose the most appropriate answer from the options given below:

(A) Both statement I and statement II are correct

(B) Statement I is incorrect but statement II is correct

(C) Both statement I and statement II are incorrect

(D) Statement I is correct but statement II is incorrect.

f - Block

13. Which one of the following lanthanoids does not form MO_2 ? [M is lanthanoid metal]

(A) Nd (B) Yb (C) Dy (D) Pr

f - Block

14. Which of the following pair is not isoelectronic species?

(At. no. Sm, 62; Er, 68: Yb, 70: Lu, 71; Eu, 63: Tb, 65; Tm, 69)

(A) Sm^{2+} and Eu^{3+}

(B) Yb^{2+} and Lu^{3+}

(C) Eu^{2+} and Tb^{4+}

(D) $\boxed{Tb^{2+} \text{ and } Tm^{4+}}$

f - Block

15. Cerium (IV) has a noble gas configuration. Which of the following is correct statement about it?

(A) It will not prefer to undergo redox reactions.

(B) It will prefer to gain electron and act as an oxidizing agent

(C) It will prefer to give away an electron and behave as reducing agent

(D) It acts as both, oxidizing and reducing agent.

$Ce^{+4} + e^- \longrightarrow Ce^{+3}$

O A

f - Block

16. The most common oxidation state of Lanthanoid elements is +3 . Which of the following is likely to deviate easily from +3 oxidation state?

(A) Ce (At. No. 58) (B) La (At. No. 57)

(C) Lu (At. No. 71) (D) Gd (At. No. 64)

Ce^{+4}

f - Block

17. The ' f ' orbitals are half and completely filled, respectively in lanthanide ions

(Given: Atomic no. Eu, 63; Sm, 62; Tm, 69; Tb, 65; Yb, 70; Dy, 66]

(A) Eu^{2+} and Tm^{2+}

(B) Sm^{2+} and Tm^{3+}

(C) Tb^{4+} and Yb^{2+}

(D) Dy^{3+} and Yb^{3+}

$Tb^{+4} = 4f^{14}$

$Yb^{+2} = 4f^{7}$

f - Block

18. Which one of the lanthanoids given below is the most stable in divalent form?

(A) Ce (Atomic Number 58)

(B) Sm (Atomic Number 62)

(C) Eu (Atomic Number 63)

(D) Yb (Atomic Number 70)

Eu^{+2}

f - Block

19. Which one amongst the following are good oxidizing agents?

A. Sm^{2+} B. Ce^{2+} C. Ce^{4+} D. Tb^{4+}

Choose the most appropriate answer from the options given below :

(A) C only (B) D only (C) A and B only (D) C and D only

Stable oxidatation state = +3

$+4 \longrightarrow +3 \longleftarrow +2$

Nishant Jindal

f - Block

20. The pair of lanthanides in which both elements have high third-ionization energy is:

(A) Dy, Gd (B) Lu,Yb (C) Eu,Yb (D) Eu, Gd

$Eu^{+2} = 4f^7$

$Yb^{+2} = 4f^{14}$

https://t.me/vjsir official