

f-BLOCK ELEMENTS

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)

Actinide series ($Z = 90 - 103$) (Th – Lr)

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 $4f^{1-14}5s^25p^65d^0-16s^2$.

Atomic Number	Element	Symbol	Outer electronic configuration	
			Atomic	+3 ion
58	Cerium	Ce	$4f^15d^16s^2$	$4f^1$
59	Praseodymium	Pr	$4f^36s^2$	$4f^2$
60	Neodymium	Nd	$4f^46s^2$	$4f^3$
61	Promethium	Pm	$4f^56s^2$	$4f^4$
62	Samarium	Sm	$4f^66s^2$	$4f^5$
63	Europium	Eu	$4f^76s^2$	$4f^6$
64	Gadolinium	Gd	$4f^75d^16s^2$	$4f^7$
65	Terbium	Tb	$4f^96s^2$	$4f^8$
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	$4f^{14}5d^16s^2$	$4f^{14}$

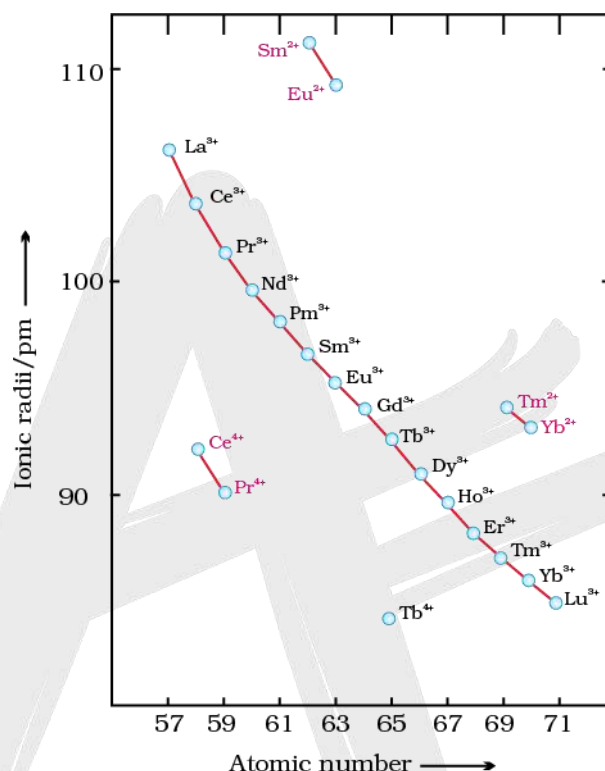
(ii) It is to be noted that filling of 4f orbitals in the atoms is not regular. A 5d electron in gadolinium ($Z = 64$) with an outer electronic configuration of $4f^7 5d^1 6s^2$ (and not $4f^8 6s^2$). This is because the 4f and 5d electrons are at about the same potential energy and that the atoms have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

Atomic and Ionic Sizes



Trends in ionic radii of lanthanoids

(i) The overall decrease in atomic and ionic radii from lanthanum to lutetium (the lanthanoid contraction) is a unique feature in the chemistry of the lanthanoids. It has far reaching consequences in the chemistry of the third transition series of the elements.

(ii) The decrease in atomic radii (derived from the structures of metals) is not quite regular as it is regular in M^{3+} ions. This contraction is, of course, similar to that observed in an ordinary transition series and is attributed to the same cause, the imperfect shielding of one electron by another in the same sub-shell. However, the shielding of one 4f electron by another is less than one d electron by another with the increase in nuclear charge along the series. There is fairly regular decrease in the sizes with increasing atomic number.

(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 :

- (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.
- (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 (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic.
- (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.

Oxidation states:

Lanthanides	Oxidation	Actinides	Oxidation state
Ce ₅₈	+3, +4	Th ₉₀	+4
Pr ₅₉	+3, (+4)	Pa ₉₁	(+4), +5
Nd ₆₀	+3	U ₉₂	(+3), (+4), (+5), +6
Pm ₆₁	+3	Np ₉₃	(+3), (+4), +5, (+6), (+7)
Sm ₆₂	(+2), +3	Pu ₉₄	(+3), +4, (+5), (+6), (+7)
Eu ₆₃	+2, +3	Am ₉₅	+2, (+3), (+4), (+5), (+6),
Gd ₆₄	+3,	Cm ₉₆	+3, (+4)
Tb ₆₅	+3, +4	Bk ₉₇	+3, (+4)
Dy ₆₆	+3, (+4)	Cf ₉₈	+3
Ho ₆₇	+3	Es ₉₉	+3
Er ₆₈	(+2), +3	Fm ₁₀₀	+3
Tm ₆₉	(+2), +3	Md ₁₀₁	+3
Yb ₇₀	+2, +3	No ₁₀₂	+3
Lu ₇₁	+3	Lr ₁₀₃	+3

(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 ($6s^2$) 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.
- (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 - Neodymium is the most paramagnetic lanthanide).
- (iii) Ce^{+4} and Yb^{+2} are also diamagnetic ions.

Colour:

- (i) The lanthanide ions have unpaired electrons in their 4f orbitals. Thus these ions absorb 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.

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

Electro positive character: 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.

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

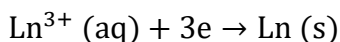
Basic Nature: $La(OH)_3$ is most basic in nature while $Lu(OH)_3$ least basic.

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

CHEMICAL PROPERTIES:

(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 :



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.

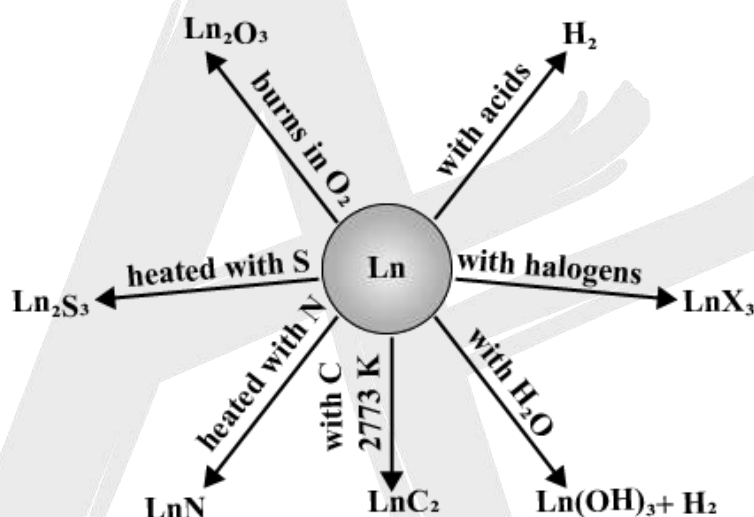
(iii) The carbides, Ln_3C , Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon.

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

(v) They form oxides M_2O_3 and hydroxides $\text{M}(\text{OH})_3$. 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.



Chemical reactions of the lanthanoids

Lanthanide contraction:

(i) In the lanthanide series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutetium or from La^{+3} to Lu^{+3} . This contraction in size is known as lanthanide contraction.

(ii) The general electronic configuration of these elements is $4f^1 - 145 s^2 p^6 d^{0-1} 6 s^2$. In these elements the added electron enters the deep seated f-orbitals and therefore experiences considerable pull by the nucleus.

(iii) Due to very poor shielding effect of $(n-2)f$ electrons, they exert very little screening effect on the outermost $6 s^2$ electrons.

Hence with increasing atomic number, the enhanced nuclear charge leads to contraction in the size of atoms and ions.

(iv) The atomic volumes of Europium and Ytterbium are unexceptably large. The large atomic size of Eu and Yb suggest weaker bonding in the solid elements. Both these elements have only two electrons extra than the stable configurations (half filled, f^7 , and completely filled, f^{14}), hence they utilise two electrons in metallic bonding as in the case with barium.

Effects of Lanthanide Contraction:

Close resemblance of Lanthanides: The general decrease in the sizes of the lanthanides with an increase in their nuclear charges result in a small increase in their ionisation energies. Hence their basic and ionic nature gradually decreases from La to Lu. This also explains the variations in properties such as increased tendency for hydrolysis and formation of complex salts and decreased thermal stability, solubility of their salts.

Similarity of Yttrium with lanthanides: The properties of Yttrium are so similar to the lanthanides that it is considered more a member of the lanthanide series than a congener of scandium.

Anomalous behaviour of post-lanthanides: The following anomalies may be observed in the behaviour of post-lanthanide elements.

(a) Atomic size: The ionic radii of Zr^{+4} is about 9% more than Ti^{+4} . Similar trend is not maintained on passing from the second to third transition series. The ionic radius of Hf^{+4} , instead of increasing (because of inclusion of one more electronic shell), decreases (or is virtually equal to Zr^{+4}) as a consequence of the lanthanide contraction. This explains the close similarities between the members of the second and third transition series than between the elements of the first and second series.

(b) Ionisation potential and electronegativity: The effect of lanthanide contraction is also seen in the increase in the ionisation potential values and electronegativities of the elements of the third transition series, contrary to the general trend. Because of the lanthanide contraction, the post-lanthanide elements have stronger positive field and thus the electrons are held more tightly. The greater effective nuclear charge of the former makes them more electronegative than the latter.

(c) High density: Because of lanthanide contraction, the atomic sizes of the post lanthanide elements become very small. Consequently, the packing of atoms in their metallic crystals become so much compact that their densities are very high. The densities of the third transition series elements are almost double to those of the second series elements.

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. $-2000^\circ C$) is used in the manufacture of a special 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 pyrophoric 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 mischmetal is used in Mg-based alloy to produce bullets, shell and lighter flint.
- 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) $\text{La}(\text{OH})_3$ is less basic than $\text{Lu}(\text{OH})_3$
(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.
3. The reason for the stability of Gd^{3+} ion is
(A) 4f subshell - half filled
(B) 4f subshell - completely filled
(C) Possesses the general electronic configuration of noble gases
(D) 4f subshell empty
4. Which of the following oxidation state is common for all lanthanoids?
(A) +2
(B) +3
(C) +4
(D) +5
5. Gadolinium belongs to 4f series. It's atomic number is 64 . Which of the following is the correct electronic configuration of gadolinium?
(A) $[\text{Xe}]4f^7 5d^1 6s^2$
(B) $[\text{Xe}]4f^6 5d^2 6s^2$
(C) $[\text{Xe}]4f^8 6d^2$
(D) $[\text{Xe}]4f^9 5s^1$

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 $\text{Np}_{93} - \text{Lr}_{103}$ 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 $5f^{1-14} 6d^{0-1} 7s^2$.

Atomic No.	Elements	Symbol	Electronic Configuration
90	Thorium	Th	$5f^0 6d^2 7s^2$
91	Protactinium	Pa	$5f^2 6d^1 7s^2$
92	Uranium	U	$5f^3 6d^1 7s^2$
93	Neptunium	Np	$5f^4 6d^1 7s^2$
94	Plutonium	Pu	$5f^6 6d^0 7s^2$
95	Americium	Am	$5f^7 6d^0 7s^2$
96	Curium	Cm	$5f^7 6d^1 7s^2$
97	Berkelium	Bk	$5f^9 6d^0 7s^2$
98	Californium	Cf	$5f^{10} 6d^0 7s^2$
99	Einsteinium	Es	$5f^{11} 6d^0 7s^2$
100	Fermium	Fm	$5f^{12} 6d^0 7s^2$
101	Mendelevium	Md	$5f^{13} 6d^0 7s^2$
102	Nobelium	No	$5f^{14} 6d^0 7s^2$
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$

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.
- (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:** Actinides are silvery white metals. They get tarnished when exposed to the attack of alkalis.
- **Density:** All the actinides except thorium and americium have high densities.

- **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 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:

- Both lanthanides and actinides show a dominant oxidation state of +3.
- Both are electropositive and act as strong reducing agents.
- Cations with unpaired electrons in both of them are paramagnetic.
- Most of the cations of lanthanides and actinides are coloured.
- Both of them show a steady decrease in their ionic radii along the series. Thus, lanthanides show lanthanide contraction and actinides show actinide contraction.

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.	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.

DO YOUR SELF -2

- There are 14 elements in actinoid series. Which of the following elements does not belong to this series?
(A) U
(B) Np
(C) Tm
(D) Fm
- 5f-subshell is filled by electron(s) -
(A) In actinides
(B) After filling of 7 s-subshell
(C) Before filling of electron in 6 d series
(D) All are correct
- Select ion which is larger than Ce^{3+}
(A) Lu^{3+}
(B) Eu^{3+}
(C) Ce^{4+}
(D) La^{3+}
- The correct order of ionic radii of Y^{3+} , La^{3+} , Eu^{3+} and Lu^{3+} is :-
(A) $\text{Y}^{3+} < \text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+}$
(B) $\text{Y}^{3+} < \text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+}$
(C) $\text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+} < \text{Y}^{3+}$
(D) $\text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+} < \text{Y}^{3+}$
- Which of the following exhibits only +3 oxidation state ?
(A) Ac
(B) Pa
(C) U
(D) Th

EXERCISE-I

- Ln (Lanthanide) $\xrightarrow[\text{Halogen}]{\text{With}}$ (X)
 Ln (Lanthanide) $\xrightarrow[\text{O}_2]{\text{Burn with}}$ (Y)
 Ln (Lanthanide) $\xrightarrow[\text{N}_2]{\Delta \text{ with}}$ (Z)
 X, Y & Z are respectively -
 (A) LnX_3 , Ln_2O_3 , Ln_3N (B) LnX_3 , Ln_2O_3 , LnN
 (C) LnX_2 , LnO , LnN (D) LnX_2 , Ln_2O_3 , Ln_3N
- Which is consequence of lanthanide contraction -
 (A) Size of Zr \gg Hf (B) Size of Zr \ll Hf
 (C) Size of Zr \approx Hf (D) Size of Zr $>$ Zr^{4+}
- Select reducing agent out of given options-
 (A) Ce^{4+} (B) Eu^{2+} (C) La^{3+} (D) Na^+
- The lanthanide contraction is responsible for the fact that :-
 (A) Zr and Y have about the same radius
 (B) Zr and Nb have similar oxidation state
 (C) Zr and Hf have about the same radius
 (D) Zr and Zn have the same oxidation state
- In the lanthanide series, the basicity of the lanthanide hydroxides
 (A) Increases (B) Decreases
 (C) First increase and then decrease (D) First decrease and then increases
- The correct order of ionic radii of Y^{3+} , La^{3+} , Eu^{3+} and Lu^{3+} is
 (A) $\text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+} < \text{Y}^{3+}$ (B) $\text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+} < \text{Y}^{3+}$
 (C) $\text{Y}^{3+} < \text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+}$ (D) $\text{Y}^{3+} < \text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+}$
- Which of the following pairs has the same size ?
 (A) Zn^{2+} , Hf^{4+} (B) Fe^{2+} , Ni^{2+} (C) Zr^{4+} , Ti^{4+} (D) Zr^{4+} , Hf^{4+}
- Which of the following ions will exhibit colour in aqueous solutions ?
 (A) Sc^{3+} (z = 21) (B) La^{3+} (z = 57)
 (C) Ti^{3+} (z = 22) (D) Lu^{3+} (z = 71)

EXERCISE-II

1. Identify the incorrect statement among the following-
(A) d-block elements show irregular and erratic chemical properties among themselves
(B) La and Lu have partially filled d-orbitals and no other partially filled orbitals
(C) The chemistry of various lanthanoids is very similar
(D) 4f and 5f-orbitals are equally shielded
2. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because
(A) The 5f-orbitals are more buried than the 4f-orbitals
(B) There is a similarity between 4f and 5f in their angular part of the wave function
(C) The actinoids are more reactive than the lanthanoids
(D) The 5f-orbitals extend further from the nucleus than the 4f-orbitals
3. Lanthanoid contraction is caused due to
(A) the same effective nuclear charge from Ce to Lu
(B) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge
(C) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge
(D) the appreciable shielding on outer electrons by 5d electrons from the nuclear charge
4. The lanthanoid contraction is responsible for the fact that -
(A) Zr and Y have about the same radius
(B) Zr and Nb have similar oxidation state
(C) Zr and Hf have about the same radius
(D) Zr and Zn have similar oxidation state
5. Cerium ($Z = 58$) is an important member of the lanthanoids. Which of the following statements about cerium is incorrect -
(A) Cerium (IV) acts as an oxidising agent
(B) The +3 oxidation state of cerium is more stable than the +4 oxidation state
(C) The +4 oxidation state of cerium is not known in solutions
(D) The common oxidation states of cerium are +3 and +4
6. The radius of La^{3+} is 1.06\AA , which of the following given values will be closest to the radius of Lu^{3+} (At no. of Lu = 71, La = 57) -
(A) 1.6\AA (B) 1.4\AA (C) 1.06\AA (D) 0.85\AA
7. Arrange Ce^{3+} , La^{3+} , Pm^{3+} and Yb^{3+} in increasing order of their ionic radius -
(A) $\text{Yb}^{3+} < \text{Pm}^{3+} < \text{Ce}^{3+} < \text{La}^{3+}$ (B) $\text{Ce}^{3+} > \text{Yb}^{3+} < \text{Pm}^{3+} < \text{La}^{3+}$
(C) $\text{Yb}^{3+} > \text{Pm}^{3+} < \text{La}^{3+} < \text{Ce}^{3+}$ (D) $\text{Pm}^{3+} < \text{La}^{3+} < \text{Ce}^{3+} > \text{Yb}^{3+}$

8. Knowing that the chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect ?
- (A) Ln (III) compounds are generally colourless
 - (B) Ln (III) hydroxides are mainly basic in character
 - (C) Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character
 - (D) The ionic sizes of Ln(III) decrease in general with increasing atomic number
9. In context of the lanthanoids, which of the following statements is not correct?
- (A) Because of similar properties the separation of lanthanoids is not easy
 - (B) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series
 - (C) There is a gradual decrease in the radii of the members with increasing atomic number in the series
 - (D) All the members exhibit +3 oxidation state

EXERCISE-III (JEE-MAIN)

- Arrange Ce^{+3} , La^{+3} , Pm^{+3} and Yb^{+3} in increasing order of their ionic radii. (2002)
 (a) $\text{Yb}^{+3} < \text{Pm}^{+3} < \text{Ce}^{+3} < \text{La}^{+3}$ (b) $\text{Ce}^{+3} < \text{Yb}^{+3} < \text{Pm}^{+3} < \text{La}^{+3}$
 (c) $\text{Yb}^{+3} < \text{Pm}^{+3} < \text{La}^{+3} < \text{Ce}^{+3}$ (d) $\text{Pm}^{+3} < \text{La}^{+3} < \text{Ce}^{+3} < \text{Yb}^{+3}$
- The radius of La^{3+} (Atomic number of La = 57) is 1.06\AA . Which one of the following given values will be closest to the radius of Lu^{3+} (Atomic number of Lu = 71)? (2003)
 (a) 1.40\AA (b) 1.06\AA (c) 0.85\AA (d) 1.60\AA
- Identify the incorrect statement among the following:
 (a) 4f and 5f orbitals are equally shielded.
 (b) d-Block elements show irregular and erratic chemical properties among themselves.
 (c) La and Lu have partially filled d-orbitals and no other partially filled orbitals.
 (d) The chemistry of various lanthanoids is very similar.
- The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because (2007)
 (a) The 5f orbitals extend further from the nucleus than the 4f orbitals
 (b) The 5f orbitals are more buried than the 4f orbitals
 (c) There is a similarity between 4f and 5f orbitals in their angular part of the wave function
 (d) The actinoids are more reactive than the lanthanoids.
- Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being (2007)
 (a) 4f orbitals more diffused than the 5f orbitals
 (b) lesser energy difference between 5f and 6d than between 4f and 5d orbitals
 (c) more energy difference between 5f and 6d than between 4f and 5d orbitals
 (d) more reactive nature of the actinoids than the lanthanoids
- Knowing that the chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect? (2009)
 (a) The ionic size of Ln (III) decreases in general with increasing atomic number
 (b) Ln (III) compounds are generally colourless.
 (c) Ln (III) hydroxides are mainly basic in character.
 (d) Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character.
- The outer electron configuration of Gd (At. No. 64) is (2011)
 (a) $4f^3 5d^5 6s^2$ (b) $4f^8 6s^2$ (c) $4f^4 5d^4 6s^2$ (d) $4f^7 5d^1 6s^2$

8. In context of the lanthanoids, which of the following statements is not correct? (2011)
(a) There is a gradual decrease in the radii of the members with increasing atomic number in the series.
(b) All the member exhibit +3 oxidation state.
(c) Because of similar properties the separation of lanthanoids is not easy.
(d) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series.
9. The maximum number of possible oxidation states of actinoids are shown by: [Main April 9, 2019]
(a) Nobelium (No) and lawrencium (Lr)
(b) Actinium (Ac) and thorium (Th)
(c) Berkelium (Bk) and californium (Cf)
(d) Neptunium (Np) and plutonium (Pu)
10. The correct order of atomic radii is: [Main Jan. 12, 2019]
(a) $N > Ce > Eu > Ho$
(b) $Ho > N > Eu > Ce$
(c) $Ce > Eu > Ho > N$
(d) $Eu > Ce > Ho > N$
11. The effect of lanthanoid contraction in the lanthanoid series of elements by and large means: [Main Jan. 10, 2019]
(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
12. The lanthanoid that does NOT show +4 oxidation state is: [Main Sep. 06, 2020]
(a) Dy (b) Ce (c) Eu (d) Tb
13. The Eu^{2+} ion is a strong reducing agent in spite of its ground state electronic configuration (outermost): [Atomic number of Eu = 63] [Main Aug. 31, 2021]
(a) $4f^7 6s^2$
(b) $4f^6$
(c) $4f^7$
(d) $4f^6 6s^2$ series of elements by and large means:

(Inorganic Chemistry)

f-BLOCK ELEMENTS

14. Arrange the following metal complex/compounds in the increasing order of spin only magnetic moment. Presume all the three, high spin system.
 (Atomic numbers Ce = 58, Gd = 64 and Eu = 63.) [Main March 16, 2021]
 (A) $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ (B) $\text{Gd}(\text{NO}_3)_3$ and (C) $\text{Eu}(\text{NO}_3)_3$
 (a) $(\text{A}) < (\text{C}) < (\text{B})$ (b) $(\text{A}) < (\text{B}) < (\text{C})$
 (c) $(\text{C}) < (\text{A}) < (\text{B})$ (d) $(\text{B}) < (\text{A}) < (\text{C})$
15. $\text{Ge}(Z = 32)$ in its ground state electronic configuration has x completely filled orbitals with $m_l = 0$. The value of x is [Main Aug. 31, 2021]
16. The number of f electrons in the ground state electronic configuration of $\text{Np}(Z = 93)$ is _____.
 (Nearest integer) [Main Aug. 27, 2021]
17. The number of f electrons in the ground state electronic configuration of electronic configuration of Gd^{2+} is _____. [Atomic number of Gd = 64] [Main Aug. 26, 2021]
18. Number of electrons present in $4f$ orbital of Ho^{3+} ion is _____.
 (Given Atomic No. of Ho = 67) [Main July. 25, 2021]
19. Given below are two statements : [Main March 16, 2021]
 Statement I: The E° value for $\text{Ce}^{4+}/\text{Ce}^{3+}$ 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 correct but statement II is incorrect
 (c) Both statement I and statement II are incorrect
 (d) Statement I is incorrect but statement II is correct
20. Which of the following pair is not isoelectronic species? [Main July 28, 2022]
 (At. no. Sm, 62; Er, 68; Yb, 70; Lu, 71; Eu, 63; Tb, 65; Tm, 69)
 (a) Sm^{2+} and Er^{3+} (b) Yb^{2+} and Lu^{3+}
 (c) Eu^{2+} and Tb^{4+} (d) Tb^{2+} and Tm^{4+}
21. 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) [Main June 27, 2022]
 (a) Eu^{2+} and Tm^{2+} (b) Sm^{2+} and Tm^{3+}
 (c) Tb^{4+} and Yb^{2+} (d) Dy^{3+} and Yb^{3+}

NCERT EXAMPLER - F-BLOCK

- Although Zirconium belongs to 4 d transition series and Hafnium to 5 d transition series even then they show similar physical and chemical properties because_____.
(A) both belong to d-block.
(B) both have same number of electrons.
(C) both have similar atomic radius.
(D) both belong to the same group of the periodic table.
- Generally transition elements and their salts are coloured due to the presence of unpaired electrons in metal ions. Which of the following compounds are coloured?
(A) KMnO_4 (B) $\text{Ce}(\text{SO}_4)_2$ (C) TiCl_4 (D) Cu_2Cl_2
- Which of the following actinoids show oxidation states upto +7 ?
(A) Am (B) Pu (C) U (D) Np
- General electronic configuration of actionoids is $(n - 2)f^{1-14}(n - 1)d^{0-2} ns^2$. Which of the following actinoids have one electron in 6 d orbital?
(A) U (Atomic no. 92) (B) Np (Atomic no.93)
(C) Pu (Atomic no.94) (D) Am (Atomic no. 95)
- Which of the following lanthanoids show +2 oxidation state besides the characteristic oxidation state +3 of lanthanoids?
(A) Ce (B) Eu (C) Yb (D) Ho
- Although +3 is the characteristic oxidation state for lanthanoids but cerium also shows +4 oxidation state because
(A) it has variable ionisation enthalpy
(B) it has a tendency to attain noble gas configuration
(C) it has a tendency to attain f^0 configuration
(D) it resembles Pb^{4+}
- Ionisation enthalpies of Ce, Pr and Nd are higher than Th, Pa and U. Why?
- Although Zr belongs to 4 d and Hf belongs to 5 d transition series but it is quite difficult to separate them. Why?
- Although +3 oxidation states is the characteristic oxidation state of lanthanoids but cerium shows +4 oxidation state also. Why?
- The second and third rows of transition elements resemble each other much more than they resemble the first row. Explain why?

11. Match the compounds/elements given in Column I with uses given in Column II.

Column I (Compound/element)

- (A) Lanthanoid oxide
(B) Lanthanoid
(C) Misch metal
(D) Magnesium based alloy is
(E) Mixed oxides of

Column II (Use)

- (i) Production of iron alloy
(ii) Television screen
(iii) Petroleum cracking
(iv) Lanthanoid metal + iron constituent of
(v) Bullets lanthanoids are employed
(vi) In X-ray screen

12. Match the statements given in Column I with the oxidation states given in Column II.

Column I

- (A) Oxidation state of Mn in MnO_2 is
(B) Most stable oxidation state of Mn is
(C) Most stable oxidation state of Mn in oxides is
(D) Characteristic oxidation state of lanthanoids is

Column II

- (i) +2
(ii) +3
(iii) +4
(iv) +5
(v) +7

13. Match the property given in Column I with the element given in Column II.

Column I (Property)

- (A) Lanthanoid which shows +4 oxidation state
(B) Lanthanoid which can show +2 oxidation state
(C) Radioactive lanthanoid
(D) Lanthanoid which has $4f^7$ electronic configuration in +3 oxidation state
(E) Lanthanoid which has $4f^{14}$ electronic configuration in +3 oxidation state

Column II (Element)

- (i) Pm
(ii) Ce
(iii) Lu
(iv) Eu
(v) Gd
(vi) Dy

Assertion and Reason Type

Note: In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (A) Both assertion and reason are true, and reason is the correct explanation of the assertion.
(B) Both assertion and reason are true but reason is not the correct explanation of assertion.
(C) Assertion is not true but reason is true.
(D) Both assertion and reason are false.

14. **Assertion:** Separation of Zr and Hf is difficult.

Reason: Because Zr and Hf lie in the same group of the periodic table.

15. **Assertion:** Actinoids form relatively less stable complexes as compared to lanthanoids.

Reason: Actinoids can utilise their 5f orbitals along with 6 d orbitals in bonding but lanthanoids do not use their 4f orbital for bonding.

16. On the basis of Lanthanoid contraction, explain the following :
- (A) Nature of bonding in La_2O_3 and Lu_2O_3
 - (B) Trends in the stability of oxo salts of lanthanoids from La to Lu
 - (C) Stability of the complexes of lanthanoids.
 - (D) Radii of 4 d and 5 d block elements.
 - (E) Trends in acidic character of lanthanoid oxides.



ANSWER KEY

Do your self - 1

Question	1	2	3	4	5
Answer	B	A	A	B	A

Do your self -2

Question	1	2	3	4	5
Answer	C	D	D	B	A

EXERCISE-I

Que.	1	2	3	4	5	6	7	8
Ans.	B	C	B	C	B	D	D	C

EXERCISE-II

Que.	1	2	3	4	5	6	7	8	9
Ans.	D	D	B	C	C	D	A	A	B

ANSWER

EXERCISE-III (JEE-MAIN)

1. (a) 2. (c) 3. (a) 4. (a) 5. (b) 6. (b)
 7. (d) 8. (d)
 9. (d) Oxidation state shown by A

Th + 3, +4

Ac + 3

Pu + 3, +4, +5, +6, +7

Np + 3, +4, +5, +6, +7

Bk + 3, +4

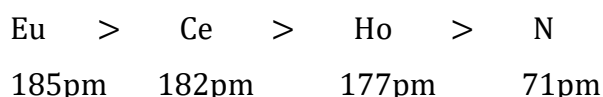
Cf + 3

L + 3

No + 3

∴ Maximum oxidation state is shown by Np and Pu.

10. (d) Atomic radii follows the order:

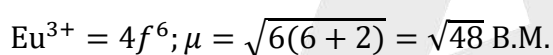
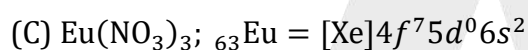
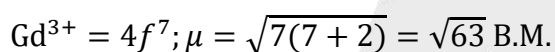
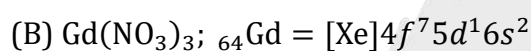
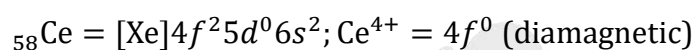
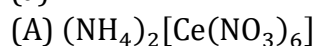


11. Due to lanthanoid contraction, size of atoms as well as ions of lanthanoid decreases.

12. (c) Europium (Eu); Atomic No. - 63 Electronic configuration - [Xe] $4f^7 6s^2$ It shows only +2 and +3 oxidation state,

13. (c) $\text{Eu} \rightarrow [\text{Xe}]4f^2 6s^2$; $\text{Eu}^{2+} \rightarrow [\text{Xe}]4f^7$

14. (a)



Order of spin only magnetic moment is

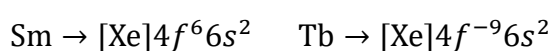
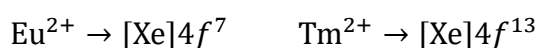
(B) > (C) > (A)

15. (b) 16. (a) 17. (d) 18. (a) 19. (c)

20. (c)

Species	Sm^{2+}	$\text{Er}^{3+}\text{Yb}^{2+}$	Lu^{3+}	Eu^{2+}	Tb^{4+}	Tb^{2+}	Tm^{4+}
No. of electrons	60	65	68	68	61	61	63

21. (c)



NCERT EXAMPLER – f – BLOCK

1. (C) 2. (A,B) 3. (B,D) 4. (A,B) 5. (B,C) 6. (B,C)
7. Hint: It is because in the beginning, when 5f orbitals begin to be occupied, they will penetrate less into the inner core of electrons. The 5f electrons will therefore, be more effectively shielded from the nuclear charge than 4f electrons of the corresponding lanthanoids. Therefore outer electrons are less firmly held and they are available for bonding in the actinoids.
8. Hint: Due to lanthanoid contraction, they have almost same size (Zr, 160pm) and (Hf, 159pm).
9. It is because after losing one more electron Ce acquires stable $4f_0$ electronic configuration.
10. Due to lanthanoid contraction, the atomic radii of the second and third row transition elements is almost same. So they resemble each other much more as compared to first row elements.
11. (A) \rightarrow (ii) ; (B) \rightarrow (i) ; (C) \rightarrow (iv) ; (D) \rightarrow (v) ; (e) \rightarrow (iii)
12. (A) \rightarrow (iii) ; (B) \rightarrow (i) ; (C) \rightarrow (v); (D) \rightarrow (ii)
13. (A) \rightarrow (ii) ; (B) \rightarrow (iv) ; (C) \rightarrow (i) ; (D) \rightarrow (v) ; (E) \rightarrow (iii)
- Assertion and Reason Type**
14. (B) 15. (C)
16. Hint: (A) As the size decreases covalent character increases. Therefore La_2O_3 is more ionic and Lu_2O_3 is more covalent.
 (B) As the size decreases from La to Lu, stability of oxosalts also decreases.
 (C) Stability of complexes increases as the size of lanthanoids decreases.
 (D) Radii of 4d and 5d block elements will be almost same.
 (E) Acidic character of oxides increases from La to Lu.