CHAPTER / 12

f-block Elements

Topics Covered

- Lanthanoids or Lanthanoid Series
- Actinoids or Actinoid Series

The elements in which the differentiating electrons enter into $(n - 2)$ f-subshell, i.e. the f-orbitals of ante-penultimate shell, are called **inner-transition elements.** Since, last electron enters into f-orbitals thus, they are known as ***f*-block elements**.

All f-block elements are metals and found rarely in earth's crust, thus they are also called **rare earth metals**. f-block elements consist of two series called lanthanoid series and actinoid series.

Lanthanoids or Lanthanoid Series

These elements follow lanthanum (La) in the periodic table and resemble, it strongly in physical and chemical properties. There are 14 elements in this series, starting with cerium, Ce ($Z = 58$) to lutetium, Lu ($Z = 71$). These are the elements in which last electron is filled in $4f$-orbital.

Properties of Lanthanoids

Some general and characteristics properties of lanthanoids are discussed below:

1. General Electronic Configuration

In general the electronic configuration of f-block elements is $[Xe]4f^{1-14}5d^{0-1}6s^2$. The electronic configuration of lanthanoids are shown in the table below:

Electronic configurations of lanthanum and lanthanoids

Atomic number	Name	Symbol	Electronic configurations (Ln)
57	Lanthanum	La	$5d^1\ 6s^2$
58	Cerium	Ce	$4f^1\ 5d^1\ 6s^2$
59	Praseodymium	Pr	$4f^3\ 6s^2$
60	Neodymium	Nd	$4f^4\ 6s^2$
61	Promethium	Pm	$4f^5\ 6s^2$
62	Samarium	Sm	$4f^6\ 6s^2$
63	Europium	Eu	$4f^7\ 6s^2$
64	Gadolinium	Gd	$4f^7\ 5d^1\ 6s^2$

Atomic number	Name	Symbol	Electronic configurations (Ln)
65	Terbium	Tb	$4f^9\ 6s^2$
66	Dysprosium	Dy	$4f^{10}\ 6s^2$
67	Holmium	Ho	$4f^{11}\ 6s^2$
68	Erbium	Er	$4f^{12}\ 6s^2$
69	Thulium	Tm	$4f^{13}\ 6s^2$
70	Ytterbium	Yb	$4f^{14}\ 6s^2$
71	Lutetium	Lu	$4f^{14}\ 5d^1\ 6s^2$

2. Atomic and Ionic Radii

The atomic and ionic radii decreases from lanthanum (La) to lutetium (Lu). This regular decrease in size of lanthanoids with increase in atomic number is known as **lanthanoid contraction**.

Cause of Lanthanoid Contraction

On moving from La to Lu in lanthanoid series, the size of atoms and ions decreases regularly. The 4*f*-orbitals containing electrons are too diffused to screen the nucleus as effectively as the more localised inner shell. Hence, the attraction of the nucleus for the outermost electrons increases steadily with increase in the atomic number. Thus, due to imperfect shielding of 4*f*-electrons, a contraction in the electron cloud of 4*f*-subshell increases, which results in contraction in size.

Consequence of Lanthanoid Contraction

(i) **Basic Character of Oxides and Hydroxides** Due to lanthanoid contraction, the basic character of oxides and hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$ due to increase in covalent nature of Ln— OH.

(ii) **Similarity in the Size or Radii of Second and Third Transition Series** Pair of elements such as Zr/Hf, Nb/Ta and Mo/W are almost identical in size due to lanthanoid contraction. Such pairs have very similar properties which make their separation difficult and hence also known as chemical twin.

(iii) **Separation of Lanthanoids** Due to lanthanoid contraction, the chemical properties of lanthanoids are similar with each other and is difficult to separate. However, lanthanoids can be separated through ion exchange method because of the small differences in some properties like solubility, degree of hydration and complex formation.

3. Oxidation State

The most common oxidation state of lanthanoids is + 3. In aqueous solution and solid state, + 3 oxidation state is more stable than other two oxidation states + 2 and + 4. This is due to the sum of ionisation and lattice energies of their tripositive ions is more negative as compared to that of + 2 and + 4 ions.

e.g. Sm^{2+}, Eu^{4+} ions loose electrons in solution to show +3 oxidation state and are good reducing agents while Ce^{4+} and Tb^{4++} gain electrons, changes to +3 oxidation and are good oxidising agents.

General Characteristics of Lanthanoids

(i) **Physical State** All lanthanoids are silvery, while soft metals which tarnish rapidly in air. Their hardness increases with increase in atomic number.

(ii) **Melting Point** Lanthanoids have high melting point (1000 K to 1200 K) with Sm as an exception that has melting point 1623 K.

(iii) **Formation of Coloured Compounds** Several trivalent (M^{3+}) lanthanide ions are coloured in solid state as well as in aqueous solution. Which arises due to *f*-*f* electronic transition, as *f*-subshells are partially filled.

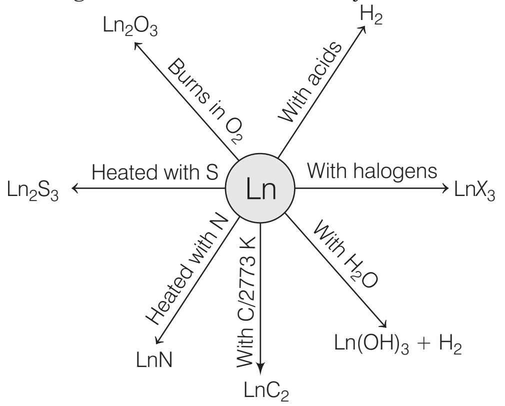
(iv) **Complex Formation** Lanthanide ions have very less tendency to form complexes. This is because of their low charge density, i.e. charge to size ratio. They form complexes with strong chelating agents like EDTA, β -diketones, oxime, etc. No complex with π-bonding ligands are known.

(v) **Alloy Formation** With other metals especially Fe they form alloys, e.g. **misch metal**, it has lanthanide metal (95%) and iron about 5% with traces of S, C, Ca and Al are used in the production of bullets, shells and lighter flint. Mixed oxides of lanthanides are used as catalysts in petroleum cracking.

(vi) **Magnetic Properties** Generally, paramagnetism is shown by lanthanoid ions except for La^{3+}, $Ce(f^0)$ and $Lu(f^{14})$. Neodymium shows maximum paramagnetism.

(vii) **Ionisation Enthalpy** The first ionisation enthalpies of lanthanoids are around 600 kJ mol^{-1}, the second about 200 kJ mol^{-1} comparable with those of calcium. The variation of the third ionisation enthalpies indicates that the exchange enthalpy consideration (as in 3*d*-orbital of 1st transition series) appears to impart a certain degree of stability to empty, half-filled and completely filled *f*-orbitals as indicated by the abnormally low third ionisation enthalpies of La, Gd and Lu.

(viii) **Chemical Behaviour** The first few members of the series are quite reactive, almost like calcium. However, with increasing atomic number, their behaviour becomes similar to that of aluminium. Following reactions are shown by lanthanoids.



Chemical reactions of the lanthanoids

Uses

(i) Lanthanoids are used for the production of alloy steels for plates and pipes.
(ii) Misch metal alloy of lanthanoid is used in Mg-based alloy to produce bullets, shell and lighter flint.
(iii) Mixed oxides of lanthanoids are used as catalyst in cracking of petroleum.
(iv) Some lanthanum oxides are used as phosphorus in television screens.

Actinoids or Actinoid Series

These elements follow actinium (Ac) upto lawrencium (Lr) and closely resemble, it physical and chemical properties. These are the elements in which last electron is filled in $5f$-orbital. They are radioactive.

Properties of Actinoids

Some properties of actinoids are discussed below:

1. General Electronic Configuration

Actinoids follow general electronic configuration of [Rn] $5f^{1-14}6d^{0-1}7s^2$.

Atomic number	Name	Symbol	Outer electronic structure	Oxidation states
89	Actinium	Ac	$6d^1\,7s^2$	III
90	Thorium	Th	$6d^2\,7s^2$	III IV
91	Protactinium	Pa	$5f^2\,6d^1\,7s^2$	III IV V
92	Uranium	U	$5f^3\,6d^1\,7s^2$	III IV V VI
93	Neptunium	Np	$5f^4\,6d^1\,7s^2$	III IV V VI VII
94	Plutonium	Pu	$5f^6\,7s^2$	III IV V VI VII
95	Americium	Am	$5f^7\,7s^2$	II III IV V V VI
96	Curium	Cm	$5f^7\,6d^1\,7s^2$	III IV
97	Berkelium	Bk	$5f^9\,7s^2$	III IV
98	Californium	Cf	$5f^{10}\,7s^2$	II III
99	Einsteinium	Es	$5f^{11}\,7s^2$	II III
100	Fermium	Fm	$5f^{12}\,7s^2$	II III
101	Mendelevium	Md	$5f^{13}\,7s^2$	II III
102	Nobelium	No	$5f^{14}\,7s^2$	II III
103	Lawrencium	Lr	$5f^{14}\,6d^1\,7s^2$	III

2. Ionic Size

The radii of trivalent and quadrivalent ions of actinoids contract slightly with increasing atomic number due to **actinoid contraction**. This contraction results from poor shielding experienced by $5f$-electrons.

3. Oxidation States

Actinoids show a variety of oxidation states due to comparable energies of $5f$, $6d$ and $7s$ energy levels. The dominant oxidation state of actinoids is $+3$ which show increasing stability for the heavier elements. The oxidation state of actinoids first increases upto the middle of the series and then decreases for the succeeding elements.

General Characteristics of Actinoids

Some important characteristics of actinoids are as follows:

(i) **Physical State** The actinoid metals are silvery soft crystals. They display variety of structure due to irregularities in metallic radii.
(ii) **Density** Actinoids have high densities in the range of 10.07 to 20.45 gkm^3.
(iii) **Melting and Boiling Points** They have high melting and boiling points,but don't show any regular trend.
(iv) **Ionisation Enthalpies** They have low ionisation enthalpies than lanthanoids because of poor shielding effect of $5f$-orbital than $4f$.
(v) **Electropositive Character** They are highly electropositive metals and hence have high tendency to lose their electrons.
(vi) **Magnetic Properties** Actinoids are strongly paramagnetic. The magnetic susceptibility of actinoids are greater than the lanthanoids.
(vii) **Colour of the Ions** Actinoid ions are generally coloured due to f-f transition. It depends upon the number of unpaired electrons in $5f$-orbitals.
(viii) **Complex Formation** Actinoids have greater tendency to form complexes due to higher nuclear charge and smaller size of their atoms.
(ix) **Chemical Behaviour** In finely divided state actinoids are highly reactive. With boiling water they give oxides and hydroxides. All these metals are good reducing agent. They react with most non-metals at normal temperature. Hydrochloric acid reacts with all these metals. However, with HNO_3 the effect is small due to formation of protective oxide layer.

Uses

(i) Actinoids (like, thorium, plutonium and uranium) are used in nuclear reactors for the production of electricity.
(ii) Actinoids are also used for the synthesis of transuranic elements.
(iii) Uranium finds applications in textiles, ceramics, medicines and to impart green colour to bulbs.

Comparison between Lanthanoids and Actinoids

Property	Lanthanoids	Actinoids
Oxidation states	They show mainly +3 oxidation state. +2 and +4 oxidation states also exist.	In addition to +3 oxidation state, actinoids also show higher oxidation states like +4, +5, +6 and +7.
Binding energies	Binding energies of $4f$ are higher.	Binding energies of $5f$ are lower.
Shielding effect	They have poor shielding effect.	They have even poor shielding effect than lanthanoids.

Magnetic properties	They are paramagnetic and their magnetic properties can be easily explained.	They are also paramagnetic, but their magnetic properties cannot be easily explained.
Chemical reactivity		
(i) Tendency to form complexes	Less	More
(ii) Radioactivity	Except promethium, these are non-radioactive substances.	These are radioactive substances.
(iii) Basic character	These are less basic.	These are more basic.
(iv) Oxidation	They do not form oxocation.	They form oxocations like UO_2^+, UP_2^+, PuO_2^{2+}.

Similarities between lanthanoids and actinoids are :
(i) Both exhibit + 3 oxidation state predominantly.
(ii) Both are electropositive and have high reactivity.
(iii) Like lanthanoid contraction, there is actinoid contraction also.
(iv) They show ion exchange behaviour.

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Exams' Questions

Q.1 The general electronic configuration of lanthanoids is ……… . **[2019]**

Sol The general electronic configuration of lanthanoids is $(n-2)\,f^{1-14}$, $(n-1)d^{0-1}$, ns^2.

Important Questions

Q.2 Which of the following has got incompletely filled f-subshell?
(a) Gadolinium (b) Lutetium
(c) Lawrencium (d) Tantalum

Sol. (*a*) Gadolinium has electronic configuration $4f^7 5d^1 6s^2$, thus it has got incompletely filled f-subshell.

Q.3 Which of the following pairs have same size? **[Textbook]**
(a) Zn^{2+}, Hf^{4+} (b) Fe^{2+}, Ni^{2+}
(c) Zr^{4+}, Ti^{4+} (d) Zr^{4+}, Hf^{4+}

Sol (*d*) Zr^{4+} and Hf^{4+} have same size due to lanthanoid contraction.

Q.4 The lanthanoid ions are coloured due to **[Textbook]**
(a) p-p transition (b) d-d transition
(c) d-f transition (d) f-f transition

Sol (*d*) The lanthanoid ions are coloured due to f-f transition.

Q.5 The atomic size of cerium and promethium is quite close, because
(a) they are in same period in periodic table
(b) their electronic configuration is same
(c) f-electrons have poor shielding effect
(d) nuclear charge is higher on cerium than promethium

Sol. (*c*) The atomic size of cerium and promethium is quite close because f-electrons have poor shielding effect.

Q.6 Outer electronic configuration of Gd (atomic number = 64) is ………

Sol. $4f^7 5d^1 6s^2$.

Q.7 Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.

Sol Europium have half-filled f-orbital in +2 oxidation state. Thus, in lanthanoid series, it exhibit +2 oxidation state.

Q.8 What is meant by 'lanthanoid contraction'?

Sol **Lanthanoid contraction** The overall decrease in atomic and ionic radii from lanthanum to lutetium, due to the imperfect shielding of one electron by another in the same subshell is known as lanthanoid contraction.

Q.9 La^{3+} $(Z = 57)$ and Lu^{3+} $(Z = 71)$ do not show any colour in solutions. Give reason.

Sol La^{3+} (lanthanum) have $4f^0$ and Lu^{3+} (lutetium) have $4f^{14}$ configuration. Because of the absence of unpaired electrons, these ions impart no colour to the solution.

Q.10 Why is europium (II) more stable than cerium (II)?

Sol Electronic configuration of Eu^{2+} is $[Xe]\,4f^7 5d^0$ and Ce^{2+} is $[Xe]\,4f^1 5d^1$. Since, Eu^{2+} have half-filled $4f^7$ configuration, therefore it is more stable than Ce^{2+} in which neither $4f$ nor $5d$-subshell are half-filled or completely filled.

Q.11 Which lanthanoid shows maximum paramagnetism? **[Textbook]**

Sol Neodymium shows maximum paramagnetism.

Q.12 Name the common mineral containing lanthanoids. **[Textbook]**

Sol Monazite

2 MARK Questions

Important Questions

Q.13 'Eu' and 'Yb' show + 2 oxidation state, whereas + 4 oxidation state is shown by Ce and Tb. Why? **[Textbook]**

Sol Refer to page 185. **(2)**

Q.14 Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

Sol. The decrease in atomic (or ionic) radii (actinoid contraction) in actinoids is greater than lanthanoid contraction because $5f$-electrons have poor shielding effect as compared to $4f$-electrons. Therefore, the effect of increased nuclear charge leading to contraction in size is more in case of actinoids. (2)

Q.15 The chemistry of the actinoid elements is not, so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.

Sol. Lanthanoids show limited number of oxidation states as +2, +3 and +4 (out of which +3 is most common). This is due to the large energy gap between $4f$ and $5d$-subshells.

The dominant oxidation state of actinoids is also +3 but they show a number of other oxidation states also, like uranium ($Z = 92$) and plutonium ($Z = 94$) show +3, +4, +5 and +6, neptunium ($Z = 93$) shows +3, + 4 +5 and +7. This is due to small energy difference between $5f$, $6d$ and $7s$-subshells of actinoids. (2)

Q.16 Calculate the spin only magnetic moment for Ce^{3+} ion. [Atomic number of Ce = 58]

Sol ${}_{58}Ce = [Xe]\,4f^1 5d^1 6s^2 \Rightarrow Ce^{3+} = [Xe] 4f^1 5d^0 6s^0$ **(1)**

Magnetic moment, $\mu = \sqrt{n\,(n+2)}$

(here, $n = 1$; n = number of unpaired electrons)

$\mu = \sqrt{1\,(1+2)} = 1.73$ BM **(1)**

3 MARK Questions

Exams' Questions

Q.17 What is lanthanoid contraction? Write any two of its consequences. **[2018]**

Sol **Lanthanoid contraction** The overall decrease in atomic and ionic radii from lanthanum to lutetium, due to the imperfect shielding of one electron by another in the same subshell, is known as lanthanide contraction. **(1)**

Consequences of lanthanide contraction are as follows :

(i) Due to lanthanoid contraction, the basic character of oxides and hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$. **(1)**

(ii) Elements of second and third d-series exhibit similar radii (e.g. Zr-160 pm, Hf-159 pm) and have very similar physical and chemical properties. **(1)**

Important Questions

Q.18 Compare the chemistry of actinoids with that of lanthanoids with special reference to **[Textbook]**

(i) electronic configuration (ii) atomic and ionic radii

(iii) oxidation states

Sol (i) Refer to text on pages 184 and 186.

(ii) Refer to text on pages 185 and 186.

(iii) Refer to text on pages 185 and 186. **(3)**

Q.19 $La(OH)_3$ is more basic than $Lu(OH)_3$, why?

(Hint : As the size of lanthanide ions decrease from La^{+3} to Lu^{3+}, the covalent character of the hydroxide increases). **[Textbook]**

Sol Refer to text on page 185. **(3)**

Q.20 What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.

Sol. An alloy is a homogeneous mixture of two or more metals or non-metals. It is prepared by blending the metals (and/or non-metal) in molten state. (1)

An important alloy containing lanthanoid metals (95%), iron (5%), traces of S, C, Ca and Al are misch metal. (1)

Misch metal is used in Mg based alloy to produce bullets, shell and lighter flint. (1)

7 MARK Questions

Important Questions

Q.21 (i) Write the general electronic configuration of lanthanoids.

(ii) Why Sm^{2+}, Eu^{2+} and Yb^{2+} ions in solutions are good reducing agents?

(iii) Why is the separation of lanthanoid elements difficult? **[Textbook]**

Sol (i) Refer to text on page 184.

(ii) Refer to text on page 185.

(iii) Refer to text on page 185. **(7)**

Q.22. (i) Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.

(ii) What is lanthanoid contraction and what is its cause? Name an important alloy which contains some of the lanthanoid metals.

Sol. (i) Lawrencium (Lr, $Z = 103$) is the last element of actinoid series. (1)

Electronic configuration

${}_{103}Lr = {}_{86}[Rn]\,5f^{14}\,6d^1\,7s^2$ **(1)**

Its possible oxidation state = + 3. **(1)**

(ii) Refer to text on page 327. (4)

Chapter Test

1 MARK *Questions*

1 The maximum oxidation state exhibited by actinide ions is **[Textbook]**
(a) + 4 (b) + 5
(c) + 7 (d) + 8

2 The most common mineral containing lanthanoids is **[Textbook]**
(a) pyrites (b) monazite sand
(c) rock salt (d) None of these

3 Misch metal is
(a) an alloy which consists of a lanthanoid metal (~95%) and iron (~5%) an traces of S, C, Ca and Al.
(b) used in Mg based alloy to produce bullets, shell and lighter flint.
(c) Both (a) and (b) are true
(d) Both (a) and (b) are false

4 Consider the following statements:
I. $La(OH)_3$ is the least basic among hydroxides of lanthanides.
II. Zr^{4+} and Hf^{4+} possess almost the same ionic radii.
III. Ce^{4+} can act as an oxidising agent.
Which of the above is/are true?
(a) I and III (b) II and III
(c) Only II (d) I and II

[*Ans.* **1.** (c), **2.** (b), **3.** (c), **4.** (b)]

5 Why do actinoids in general exhibit a greater range of oxidation states than the lanthanoids?

6 Account for the following :
There are irregularities in the electronic configuration of actinoids.

7 Write down the electronic configuration of
(i) Lu^{2+} (ii) Pm^{3+} **[Textbook]**

8 An element X is a radioactive element. In which part of periodic table, the element should reside?

2 MARK *Questions*

9 Write one similarity and one difference between the chemistry of lanthanoids and that of actinoids.

10 Explain,
(i) the atomic size of cerium and promethium is quite similar.
(ii) shielding power of $4f$-electrons is quite poor.

11 Mention important uses of uranium and plutonium. **[Textbook]**

12 Give reason. Why in chemistry of all the lanthanoids is quite similar? **[Textbook]**

3 MARK *Questions*

13 Yb^{2+} acts as a reductant, while Tb^{4+} act as an oxidant. Why?

14 Account for the following:
(i) Paramagnetism is shown by lanthanoid ions. Comment.
(ii) Compare the basic strength of $Ln(OH)_3$, $Ca(OH)_2$ and $Al(OH)_3$.
(iii) Lanthanoids do not form their carbonyl compounds.

7 MARK *Questions*

15 Why Sm^{2+}, Eu^{2+} and Yb^{2+} ions in solutions are good reducing agents, but an aqueous solution of Ce^{4+} is a good oxidising agent. **[Textbook]**

16 Compare the chemistry of actinoids with that of lanthanoids with special reference to
(i) electronic configuration **[Textbook]**
(ii) oxidation state
(iii) atomic and ionic sizes
(iv) chemical reactivity

17 Explain the following:
(i) The metallic radii of the third ($5d$) series of transition metals are virtually the same as those of the corresponding group member of the second ($4d$) series.
(ii) La^{3+} and Lu^{3+} are colourless, whereas Sm^{3+} and Eu^{3+} are coloured.
(iii) Shielding power of $4f$-electrons is quite poor.