

f-BLOCK ELEMENTS

1. INTRODUCTION

1.1 Inner transition elements/f-block elements

The elements in which the additional electrons enter $(n - 2)f$ orbitals are called inner transition elements. The valence shell electronic configuration of these elements can be represented as $(n-2)f^{0,2,\dots,14}(n-1)d^{0,1,2}ns^2$. These are also called as f-block elements because the extra electrons go to f-orbitals which belong to $(n-2)$ th main shell. 4f-block elements are also called Lanthanides or rare earths. Similarly, 5f-block elements are called actinides or actinones. The name Lanthanides and Actinides have been given due to close resemblance with Lanthanum and Actinium respectively. Lanthanides constitute the first inner transition series while actinides constitute the second inner transition series.

General Characteristics:

- 1. Electronic Configuration :** $[\text{Xe}] 4f^{n+1}5d^06s^2$ or $[\text{Xe}] 4f^n5d^16s^2$
- 2. Oxidation state:** They readily form M^{+3} ions. Some of them also exhibit oxidation states of +2 and +4.
- 3. Colouration:** Ions of Lanthanides and Actinides are coloured in the solid state as well as in aqueous solution because of absorption of light due to f-f-transition, since they have partly filled f-orbitals.

Magnetic properties: $\text{La}^{3+}(4f^0)$ and $\text{Lu}^{3+}(4f^{14})$ having no unpaired electrons do not show paramagnetism while all other tri-positive ions of lanthanides are paramagnetic

Illustration 14: What is the basic difference between the electronic configuration of transition and inner transition elements. **(JEE MAIN)**

Sol: General electronic configuration of transition elements = $[\text{Noble gas}] (n - 1) d^{1-10}ns^{1-2}$ and for inner transition elements = $(n - 2) f^{1-14}(n - 1)d^{0-1}ns^{0-2}$. Thus, in transition elements, the last electron enters d-orbitals of the penultimate shell while in inner transition elements, it enters f-orbitals of the penultimate shell.

Illustration 15: What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements: 29, 59, 74, 95, 102, 104. **(JEE MAIN)**

Sol: Inner transition elements are those which have incomplete 4f or 5f orbitals. Thus 59, 95 and 102 are inner transition elements.

2. LANTHANIDES AND THEIR PROPERTIES

The lanthanide series of chemical elements comprises the fifteen metallic chemical elements with atomic numbers 57 through 71, from lanthanum through lutetium. These fifteen lanthanide elements, along with the chemically similar elements, scandium and yttrium, are often collectively known as the rare earth elements.

2.1 Lanthanide Contraction

In lanthanides, the additional electron enters the 4f-sub shell but not in the valence-shell i.e. sixth shell. The shielding effect of one electron in 4f-sub-shell by another in the same sub-shell is very little, being even smaller than that of d-electrons, because the shape of f-sub shell is very much diffused, while there is no comparable increase in the mutual shielding effect of 4f-electrons. This results in outermost shell electrons experiencing increasing nuclear attraction from the growing nucleus. Consequently, the atomic and ionic radii go on decreasing as we move from La_{57} to Lu_{71} .

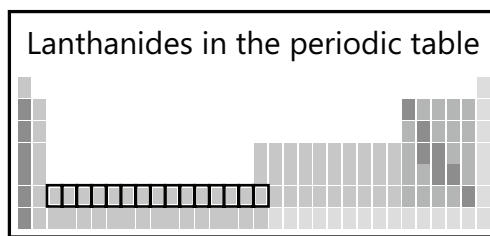


Figure 31.4: Position of lanthanides in the periodic table

Consequence of Lanthanide contraction

- 1. Atomic and ionic radii of post-Lanthanide elements:** The atomic radii of second row transition elements are almost similar to those of the third row transition elements because the increase in size on moving down the group from second to third transition elements is cancelled by the decrease in size due to lanthanide contraction.
- 2. High density of post Lanthanide elements:** It is because of a very small size due to lanthanide contraction and increase in molar mass.
- 3. Basic strength of oxides and hydroxides:** Due to lanthanide contraction, the decrease in size of lanthanides ions, from La^{3+} to Lu^{3+} increases the covalent character (i.e. decreases the ionic character) between Ln^{+3} and OH^- ions in $\text{Ln}(\text{III})$ hydroxides (Fajan's rules). Thus $\text{La}(\text{OH})_3$ is the most basic while $\text{Lu}(\text{OH})_3$ is the least basic. Similarly, there is a decrease in the basic strength of the oxides.
- 4. Separation of Lanthanides:** Due to the similar size (lanthanide contraction) of the lanthanides, it is difficult to separate them. But a slight variation in their properties is utilized to separate.

MASTERJEE CONCEPTS

The existence of lanthanoids in oxidation state of +2 and +4 is due to the fact that empty, half-filled or completely filled f-subshells provide lower energy levels and the ions get stabilized. For example, Ce and Tb show +4 oxidation state by attaining stable f^0 and f^7 configuration respectively whereas Eu and Yb show +2 oxidation state by attaining stable f^7 and f^{14} configuration, respectively.

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Illustration 16: Why is the separation of lanthanoids difficult? Explain.

(JEE MAIN)

Sol: All the Lanthanoid ions are of almost the same size, so they have almost similar chemical and physical properties and thus their separation becomes difficult.

Illustration 17: Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behavior with the electronic configuration of these elements.

(JEE MAIN)

Sol: +4 = Ce, Pr, Nd, Tb, Dy. +2 = Eu, Yb. These states are accounted by the extra stability of half-filled and completely filled f-orbitals.

2.2 Chemical Reactivity

These are very reactive metals like alkaline earth metals, however, they show very little difference in their chemical reactivity. On strong heating with H_2 and carbon, these form salt like non-stoichiometric hydrides and carbides. They burn in oxygen to give sesquioxides M_2O_3 (except Ce which gives CeO_2). Their ionic oxides react with water to form

insoluble hydroxides. The oxides and hydroxides being strong base react with CO_2 to form carbonates (M_2CO_3). On burning in sulphur these form sulphides (M_2S_3).

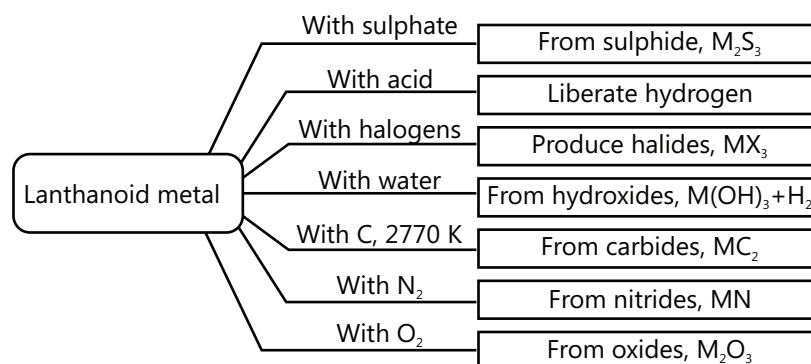


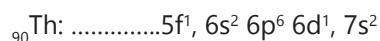
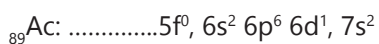
Figure 31.5: Chemical reactivity of lanthanoid metal

2.3 Uses of Lanthanoids

- (i) Pyrophoric alloys, known as **Misch metals**, contain lanthanoids about 90-95% (Ce 40.5%, lanthanum and neodymium 44%), iron 4.5%, calcium, carbon and silicon about 10.5% are used in cigarette and gas lighters, flame throwing tanks, toys, tank and tracer bullets as well as in shells.
- (ii) Any alloy containing 30% Misch metals and 1% Zr are used for making parts of jet engines.
- (iii) Cerium salts are commonly used as catalyst in petroleum cracking (cerium phosphate), volumetric analysis and as oxidizing agent (ceric sulphate), in dyeing cotton, in lead accumulators etc,
- (iv) Oxides of praseodymium (Pr_2O_3) and neodymium (Nd_2O_3) are used in the preparation of coloured glasses and standard filters.
- (v) Oxides of cerium and thorium are used in the preparation of gas lamp mantles.
- (vi) Cerium oxide is used to prepare sunglasses as cerium cuts off heat and ultraviolet light.

3. ACTINIDES AND THEIR PROPERTIES

- (i) The differentiating electron occupies 5f-subshell and thus these elements also have three outermost shells not filled to their capacity. These are called actinoids or actinones.



- (ii) The electronic configuration of actinoids is $[\text{Rn}] 5f^{0-14}, 6d^{0-2}, 7s^2$ where [Rn] stands for radon core. Like lanthanoids, they are placed together because of similar chemical nature.
- (iii) Like lanthanoids contraction, these too show actinoid contraction due to poor shielding effect of 5f-subshells. Thus, atomic size of actinoids too decreases gradually from Ac to Lw.
- (iv) Actinoids show a range of oxidation states, which is due to comparable energies of 5f, 6d and 7s-orbitals. The general oxidation state of actinoids is +3; the elements in the first half of the series show higher oxidation states.
- (v) All these elements are strong reducing agents and are very reactive metals. Actinoids are radioactive and, therefore, it is difficult to study their chemical nature. However, relatively more stable isotopes of these elements beyond uranium have been discovered and the chemistry of these elements has been studied to an extent by using radiotracer techniques.

Like lanthanoids, they react with oxygen, halogens, hydrogen, sulphur and acids.

Uses of Actinoids: Only U, Th have found applications in nuclear reactions undergoing nuclear fission to produce nuclear power and nuclear bombs.

MASTERJEE CONCEPTS

The 5f orbitals extend in space beyond 6s and 6p orbitals and participate in bonding.

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Illustration 18: The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. **(JEE MAIN)**

Sol: This difference is due to occurrence of a wide range of oxidation states in actinoids. Also, their radioactivity causes a hindrance in their study.

POINTS TO REMEMBER

- General electronic configuration of d-block elements is $(n-1)d^{1-10}ns^{0,1,2}$ and that of f-block element is $(n-2)f^{0,2,....,14}(n-1)d^{0,1,2}ns^2$
- Their melting and boiling points are high which are attributed to the involvement of $(n-1)d$ electrons resulting in strong metallic bonds.
- Successive ionisation enthalpies do not increase as steeply as in the main group elements with increasing atomic number. Hence, the loss of variable number of electrons from $(n-1)d$ orbitals is not energetically unfavourable.
- Ionisation energies where the electron is removed from half-filled or completely filled orbitals are especially large. Hence, Zn^{3+} is not formed.
- The metals, in addition to variable oxidation states, they exhibit paramagnetic behaviour, catalytic properties and tendency for the formation of coloured ions, interstitial compounds and complexes.
- Reactivity of these elements is calculated as a sum of heat of sublimation, ionization enthalpy as well as heat of hydration.
- The transition elements are sufficiently electropositive to dissolve in mineral acids. Of the first series, with the exception of copper, all the metals are relatively reactive.
- The transition metals react with a number of non-metals like oxygen, nitrogen, sulphur and halogens to form binary compounds. The first series transition metal oxides are generally formed from the reaction of metals with oxygen at high temperatures.
- These oxides dissolve in acids and bases to form oxometallic salts.
- The two series of inner transition elements, lanthanoids and actinoids constitute the f-block of the periodic table. With the successive filling of the inner orbitals, 4f, there is a gradual decrease in the atomic and ionic sizes of these metals along the series (lanthanoid contraction). This has far reaching consequences in the chemistry of the elements succeeding them.
- Lanthanum and all the lanthanoids are rather soft white metals. They react easily with water to give solutions giving +3 ions. The principal oxidation state is +3, although +4 and +2 oxidation states are also exhibited by some occasionally.