THE D-AND F-BLOCK ELEMENTS
THE LANTHANOIDS

❖ **THE LANTHANOIDS f - BLOCK ELEMENTS**
THE INNER TRANSITION ELEMENTS (f-BLOCK)
INTRODUCTION

The elements constituting the f-block are those in which the 4f and 5f orbitals are progressively filled. These elements are the members of group 3.

The f-block elements comprise of the two series,

(i) lanthanoids (the fourteen elements following lanthanum)

(ii) actinoids (the fourteen elements following actinium). It is important to note that the lanthanoids resembles one another more closely than that of the ordinary transition elements in any series. Lanthanoids have only one stable oxidation state and their chemical properties provide the excellent opportunity to observe the effect of small changes in size and nuclear charge along a series of similar elements. On the other hand, the chemistry of actinoids is much more complicated and this complication arises partly owing to the occurrence of a wide range of oxidation states in these elements and partly because of their radioactive nature.

LANTHANOIDS (4f - SERIES) :

Electronic configuration: The atoms of these elements have electronic configuration with $6s^2$ common but with variable occupancy of 4f level. However, the electronic configurations of all the tripositive ions which is the most stable oxidation state of all the lanthanoids, are of the form $4f^n$ (n = 1 to 14 with increasing atomic number)

Atomic sizes: There is decrease in atomic and ionic radii from lanthanum to lutetium due to lanthanoid contraction. The decrease in atomic radii is not quit regular as it is regular in M^{3+} ion. This contraction is of course, similar to that observed in an ordinary transition series and is attributed to the imperfect shielding of one electron by another in the same subshell. However, the shielding of one 4f electron by another is less than a 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.

The cumulative effect of the contraction of the lanthanoids series, known as lanthanoids 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 (159 pm) is a result of the lanthanoid contraction. This accounts for their occurrence together in nature and for the difficulty in their separation.

Oxidation state: In the lanthaoids, La(III) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or filled f subshell. Thus, the formation of Ce^{IV} is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The E° value for Ce^{4+}/Ce^{3+} is + 1.74 V which suggests that it can oxidize water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent; Pr Nd, Tb and and Dy also exhibit +4 state but only in oxides, MO_2. Eu^{2+} is formed by losing the two s electrons and its f^7 configuration accounts for the formation of this ion. However, Eu^{2+} is a strong reducing agent changing to the +3 common oxidation state. Similarly Yb^{+2} which has f^{14} configuration is a reductant. Tb^{IV} has half-filled f-orbitals and is an oxidant. The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states.

- **GENERAL CHARACTERISTICS**

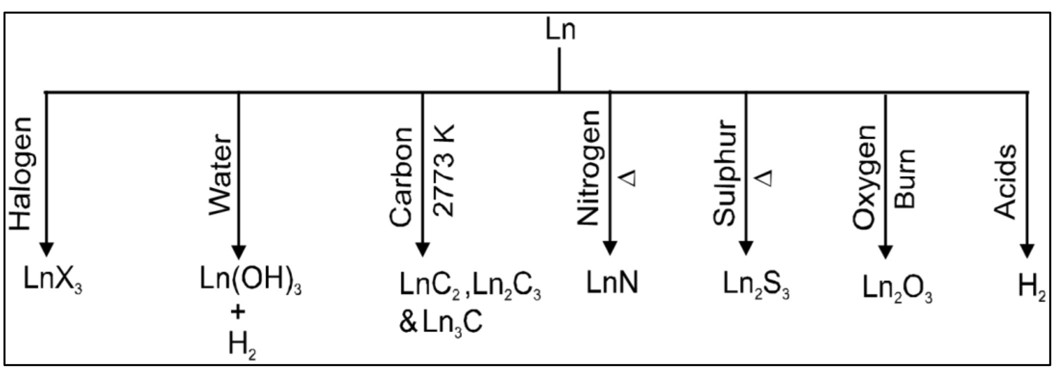
All the lanthanoids are silvery white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number, samarium is hard as steel. Their melting points range between 1000 to 1200 K but samarium melts at 1623 K. They have typical metallic structure and are good conductors of heat and electricity. Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm. Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solution. Colour of these ions may be attributed to the presence of f electron. 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. The lanthanoids ions other than the f° type (La^{+3} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetic rises to maximum in neodymium.

The first ionisation enthalpies of the lanthanoids are around 600 kJ mol^{-1}s, the second about 1200 kJ mol^{-1} comparable with those of calcium. A detailed discussion of the variation of the third ionisation enthalpies indicates that the exchange enthalpy considerations (as in 3d 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.

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 aluminum. Values for E^{θ} for the half reaction

$$Ln^{3+}(aq) + 3e^{-1} \rightarrow Ln(s)$$

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. The metals combine with hydrogen when gently heated in the gas. They form oxides M_2O_3 and hydroxides $M(OH)_3$. The hydroxides are definite compounds, not just hydrate oxides. They are basic like alkaline earth metals oxides and hydroxides.



USES OF LANTHANOIDS

1. Used for the production of alloy steels for plates and pipes. e.g., mischmetal which consists of lanthanoid metal (~95%) and iron (~5%) and traces of S, C, Ca and Al. Mischmetall is used in Mg based alloy to produce bullets, shell and lighter flint.

2. Mixed oxides of lanthanoids are employed as catalyst in petroleum cracking.
3. Some individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.
4. Because of their paramagnetic and ferromagnetic character, their compounds are used in making magnetic & electronic devices.
5. Ceric sulphate is a well-known oxidizing agent in volumetric analysis.