THE D-AND F-BLOCK ELEMENTS
THE LANTHANOIDS

THE LANTHANOIDS f - BLOCK ELEMENTS

THE INNER TRANSITION ELEMENTS (f-BLOCK)

INTRODUCTION

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

The f-block elements encompass two series:

(i) Lanthanoids, which consist of the fourteen elements following lanthanum.

(ii) Actinoids, which comprise the fourteen elements succeeding actinium. It is noteworthy that the lanthanoids exhibit a closer resemblance to each other than the ordinary transition elements in any series. Lanthanoids possess only one stable oxidation state, and their chemical properties offer an excellent opportunity to observe the effects of slight changes in size and nuclear charge along a series of similar elements. Conversely, the chemistry of actinoids is much more intricate, mainly due to the occurrence of a broad range of oxidation states in these elements and their radioactive nature.

LANTHANOIDS (4f - SERIES):

Electronic configuration: The atoms of these elements share a common electronic configuration with $6s^2$ but exhibit variable occupancy of the 4f level. However, the electronic configurations of all the Tri positive ions, which represent the most stable oxidation state for all lanthanoids, follow the pattern 4fn (where n ranges from 1 to 14, increasing with atomic number).

Atomic sizes: The decrease in atomic and ionic radii from lanthanum to lutetium is attributed to the lanthanoid contraction. While the reduction in atomic radii is not entirely regular, it is more consistent in M^{3+} ions. This contraction, similar to that observed in an ordinary transition series, results from imperfect shielding of one electron by another in the same subshell. However, the shielding of one 4f electron by another is less effective than that of a d-electron by another, leading to a gradual decrease in sizes with increasing atomic number along the series.

The cumulative impact of the lanthanoid contraction, collectively termed the lanthanoid contraction, causes the radii of the third transition series members to closely resemble those of the corresponding members in the second series. The nearly identical radii of Zr (160 pm) and Hf (159 pm) are a consequence of the lanthanoid contraction, explaining their co-occurrence in nature and the challenges in their separation.

Oxidation state: In the lanthanoids, La (III) and Ln (III) compounds are the predominant species. However, there are occasional instances of +2 and +4 ions being obtained in solution or solid compounds. This irregularity, similar to ionization enthalpies, primarily stems from the extra stability of empty, half-filled, or filled f subshells. Consequently, the formation of Ce^{IV} is favored due to its noble gas configuration, although it acts as a strong oxidant, reverting to the common +3 state. The E° value for Ce^{4+} / Ce^{3+} is +1.74 V, suggesting its potential to oxidize water. However, the reaction rate is very slow, making $Ce^{(IV)}$ a valuable analytical reagent. Pr, Nd, Tb, and Dy also exhibit the +4 state, but only in oxides (MO_2). Eu^{2+} is formed by the loss of two s electrons, and its f^7 configuration explains the formation of this ion. However, Eu^{2+} acts as a strong reducing agent, transitioning to the common +3 oxidation state. Similarly, Yb^{2+} with an f^{14} configuration is a reductant. $Tb^{(IV)}$ possesses half-filled f-orbitals and acts as an oxidant. The behavior of samarium closely resembles europium, displaying both +2 and +3 oxidation states.

GENERAL CHARACTERISTICS

All lanthanoids exhibit silvery-white, soft metal characteristics and tarnish rapidly in the air. Hardness increases with rising atomic number, with samarium being as hard as steel. Their melting points range from 1000 to 1200 K, but samarium melts at 1623 K. Possessing a typical metallic structure, they are effective conductors of heat and electricity. Density and other properties generally change smoothly, except for Eu and Yb, and occasionally for Sm and Tm.

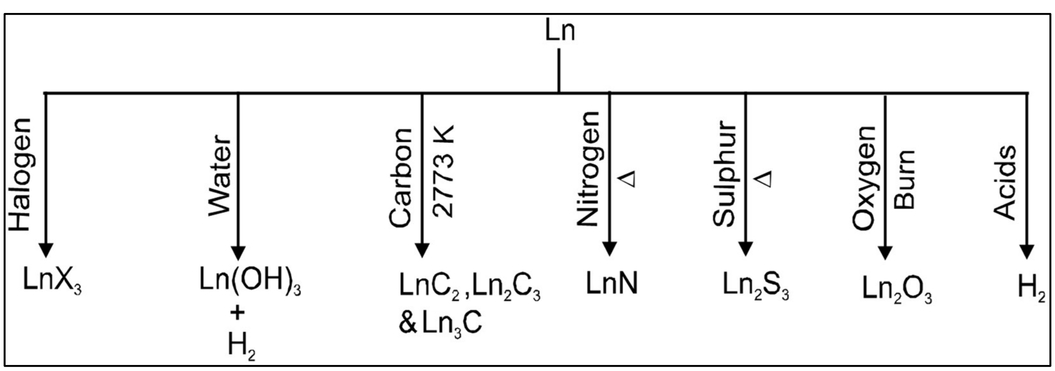
Many trivalent lanthanoid ions display coloration in both the solid state and aqueous solutions. The color of these ions may be attributed to the presence of f electrons. Neither La^{3+} nor Lu^{3+} ions exhibit any color, but the rest do. However, absorption bands are narrow, likely due to excitation within the f level. Lanthanoid ions, aside from the f° type (La^{3+} and Ce^{4+}) and the f14 type (Yb^{2+} and Lu^{3+}), are all paramagnetic, with the Para magnetism peaking in neodymium.

The first ionization enthalpies of lanthanoids are around 600 kJ mol^{-1}, with the second around 1200 kJ mol^{-1}, comparable to those of calcium. A detailed exploration of the variation in third ionization enthalpies indicates that exchange enthalpy considerations, similar to the 3d orbitals of the first transition series, seem to provide a certain degree of stability to empty, half-filled, and completely filled orbitals in the f level. This is evident from the abnormally low values of the third ionization enthalpies 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. Utilized in the production of alloy steels for plates and pipes, for instance, mischmetal, comprising lanthanoid metals (~95%), iron (~5%), and traces of S, C, Ca, and Al. Mischmetal is employed in magnesium-based alloys to manufacture bullets, shells, and lighter flints.
2. Mixed oxides of lanthanoids serve as catalysts in petroleum cracking.
3. Individual lanthanoid oxides find application as phosphors in television screens and similar fluorescing surfaces.
4. Due to their paramagnetic and ferromagnetic characteristics, compounds of lanthanoids are employed in the manufacturing of magnetic and electronic devices.
5. Ceric sulfate is a well-known oxidizing agent in volumetric analysis.