The *d*- and *f*- Block Elements - Part 4

Objectives

After going through this lesson, the learners will be able to understand the following:

- Write the electronic configurations of the inner transition (*f*- block) elements and their ions;
- Explain the general characteristics of the *f*-block elements (lanthanoids and actininoids) and the general horizontal and group trends in them;
- Describe the properties of the *f*-block elements and give a comparative account of the lanthanoids and actinoids with respect to their electronic configurations, oxidation states and chemical behaviour.

Contents Outline

- General Introduction: Inner Transition Elements (*f*- block)
- The Lanthanoids
    - Properties of Lanthanoids
    - Electronic Configuration
    - Atomic and Ionic sizes
    - Oxidation States
    - General Characteristics
- The Actinoids
    - Properties of Actinoids
    - Electronic Configuration
    - Ionic Sizes
    - Oxidation States
    - General Characteristics & Comparison with Lanthanoids
- Applications of *d*- and *f*- Block Elements
- Summary

The Inner Transition (*f*- block) Elements

The f-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium). Because lanthanum closely resembles the lanthanoids, it is usually included in any discussion of the lanthanoids for which the general symbol Ln is often used. Similarly, a discussion of the actinoids includes actinium besides the fourteen elements constituting the series. The lanthanoids resemble one another more closely than do the members of ordinary transition elements in any series. They have only one stable oxidation state and their chemistry provides an excellent opportunity to examine the effect of small changes in size and nuclear charge along a series of otherwise similar elements. The chemistry of the actinoids is, on the other hand, much more complicated. The complication arises partly owing to the occurrence of a wide range of oxidation states in these elements and partly because their radioactivity creates special problems in their study; the two series will be considered separately here.

The Lanthanoids

The names, symbols, electronic configurations of atomic and some ionic states and atomic and ionic radii of lanthanum and lanthanoids (for which the general symbol Ln is used) are given in Table 1.

Table 1. Electronic Configurations and Radii of Lanthanum and Lanthanoids

Atomic Number	**Name of Element**	**Symbol**	**Electronic Configuration**			**Oxidation States**	**Radii /pm**	
			Ln	**Ln^{2+}**	**Ln^{3+}**		**Ln**	**Ln^{3+}**
57	Lanthanum	La	$5d^1 6s^2$	$5d^1$	$4f^0$	+3	187	106
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^2$	$4f^1$	+3, +4	183	103
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^3$	$4f^2$	+3, +4	182	101
60	Neodymium	Nd	$4f^4 6s^2$	$4f^4$	$4f^3$	+2, +3, +4	181	99
61	Promethium	Pm	$4f^5 6s^2$	$4f^5$	$4f^4$	+3	181	98
62	Samarium	Sm	$4f^6 6s^2$	$4f^6$	$4f^5$	+2, +3	180	96
63	Europium	Eu	$4f^7 6s^2$	$4f^7$	$4f^6$	+2, +3	199	95
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7 5d^1$	$4f^7$	+3	180	94

65	Terbium	Tb	$4f^9 6s^2$	$4f^9$	$4f^8$	+3, +4	178	92
66	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^{10}$	$4f^9$	+3, +4	177	91
67	Holmium	Ho	$4f^{11} 6s^2$	$4f^{11}$	$4f^{10}$	+3	176	89
68	Erbium	Er	$4f^{12} 6s^2$	$4f^{12}$	$4f^{11}$	+3	175	88
69	Thulium	Tm	$4f^{13} 6s^2$	$4f^{13}$	$4f^{12}$	+2, +3	174	87
70	Yitterbium	Yb	$4f^{14} 6s^2$	$4f^{14}$	$4f^{13}$	+2, +3	173	86
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14} 5d^1$	$4f^{14}$	+3	-	-

only electrons outside [Xe] core are indicated

- **Electronic Configuration**

  All lanthanoids have electronic configuration with $6s^2$ common but with variable occupancy of $4f$ level in their atoms (Table 1). However, the electronic configuration of all the tri-positive ions (the most stable oxidation state of all the lanthanoids) is of the form $4f^n$ (n = 1 to 14 with increasing atomic number).

- **Atomic and Ionic sizes**

  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. The decrease in atomic radii (derived from the structures of metals) is not quite regular while decrease in ionic radii (M^{3+}) is regular (Fig. 1). 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 a fairly regular decrease in the sizes with increasing atomic numbers.

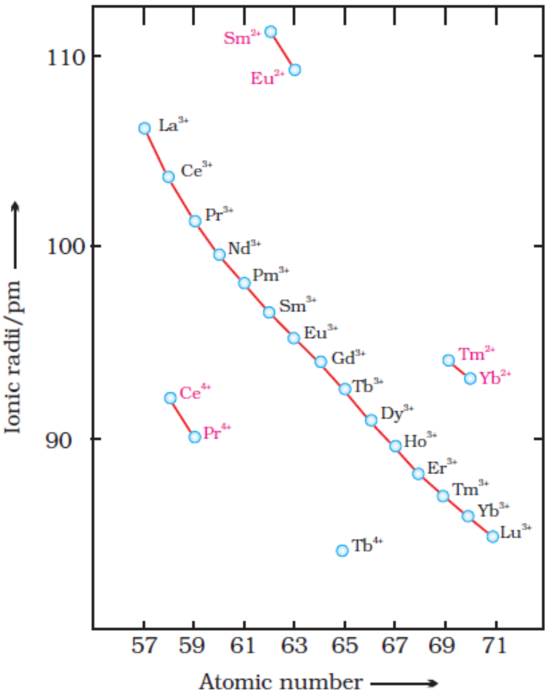

Fig. 1. Trends in ionic radii of lanthanoids

(Source: Fig. 8.6, page no. 228, Chapter 8, Chemistry Textbook, NCERT)

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 (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

- **Oxidation States**

  The possible stable oxidation states of the lanthanoids are tabulated in Table 1. In the lanthanoids, 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^{Θ} value for Ce^{4+} /Ce^{3+} is + 1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent. Pr, Nd, Tb 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 common +3 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**
    - ***Physical State*:** All the lanthanoids are silvery white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number, samarium being steel hard. Their melting points vary 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.

    - ***Colour & Magnetic Property*:** Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the excitation of *f* electrons on absorption of light in the visible region. 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 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. The orbital motions of the electrons in lanthanoids are not quenched, so both spin and orbital angular momentum contribute towards μ. This is in contrast to metal ions of the first transition series where the 'spin only' formula is used.

    - ***Ionisation Enthalpy*:** 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 ionisation 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.
    - ***Chemical Reactivity*:** 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° for the half-reaction:

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

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. The carbides, Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon. They liberate hydrogen from dilute acids and burn in halogens to form halides. They form oxides M_2O_3 and hydroxides $M(OH)_3$. The hydroxides are definite compounds, not just hydrated oxides. They are basic like alkaline earth metal oxides and hydroxides. Their general reactions are depicted in Fig. 2.

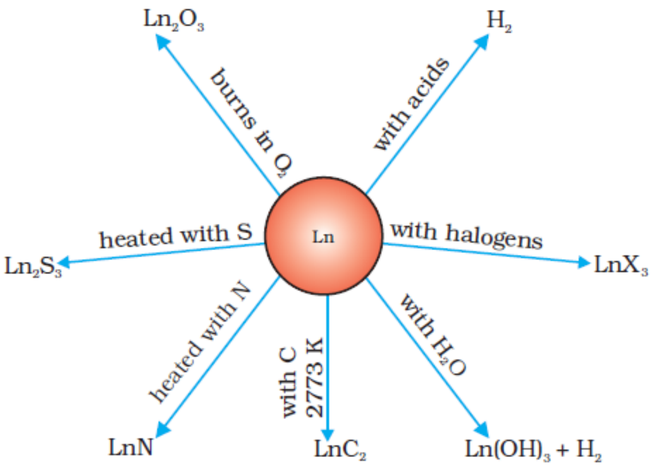

Fig. 2. Chemical reactions of the lanthanoids

(Source: Fig. 8.7, page no. 230, Chapter 8, Chemistry Textbook, NCERT)

Uses: The best single use of the lanthanoids is for the production of alloy steels for plates and pipes. A well known alloy is mischmetal which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A good deal of mischmetal is used in Mg-based alloy to produce bullets, shells 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.

The Actinoids

The actinoids include the fourteen elements from Th to Lr. The names, symbols and some properties of these elements are given in Table 2. The actinoids are radioactive elements and the earlier members have relatively long half-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium (Z =103). The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

Table 2. Electronic Configurations and Radii of Actinium and Actinoids

Atomic Number	**Name of Element**	**Symbol**	**Electronic Configuration**			**Radii /pm**	
			M	**M^{3+}**	**M^{4+}**	**M^{3+}**	**M^{4+}**
89	Actinium	Ac	$6d^1 6s^2$	$5f^0$		111	
90	Thorium	Th	$6d^2 7s^2$	$5f^1$	$4f^0$		99
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	$5f^2$	$4f^1$		96
92	Uranium	U	$5f^3 6d^1 7s^2$	$5f^3$	$4f^2$	103	93
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$	$4f^3$	101	92
94	Plutonium	Pu	$5f^6 7s^2$	$5f^5$	$4f^4$	100	90
95	Americium	Am	$5f^7 7s^2$	$5f^6$	$4f^5$	99	89
96	Curium	Cm	$5f^7 6d^1 7s^2$	$5f^7$	$4f^6$	99	88
97	Berkelium	Bk	$5f^9 7s^2$	$5f^8$	$4f^7$	98	87
98	Californium	Cf	$5f^{10} 7s^2$	$5f^9$	$4f^8$	98	86
99	Einsteinium	Es	$5f^{11} 7s^2$	$5f^{10}$	$4f^9$	-	-
100	Fermium	Fm	$5f^{12} 7s^2$	$5f^{11}$	$4f^{10}$	-	-
101	Mendelevium	Md	$5f^{13} 7s^2$	$5f^{12}$	$4f^{11}$	-	-
102	Nobelium	No	$5f^{14} 7s^2$	$5f^{13}$	$4f^{13}$	-	-
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	$5f^{14}$	$4f^{13}$	-	-

Properties of Actinoids

- **Electronic Configuration:** All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of the $5f$ and $6d$ subshells. The fourteen electrons are formally added to $5f$, though not in thorium (Z = 90) but from Pa onwards the 5f orbitals are complete at element 103. The irregularities in the electronic configurations of the actinoids, like those in the lanthanoids are related to the stabilities of the f^0, f^7 and f^{14} occupancies of the 5*f* orbitals. Thus, the configurations of Am and Cm are [Rn] $5f^7\ 7s^2$ and [Rn] $5f^7\ 6d^1\ 7s^2$. Although the 5*f* orbitals resemble the 4*f* orbitals in their angular part of the wave-function, they are not as buried as 4*f* orbitals and hence 5*f* electrons can participate in bonding to a far greater extent.

- **Ionic sizes:** The general trend of lanthanoids is observable in the actinoids as well. There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the *actinoid contraction* (like *lanthanoid contraction*). The contraction is, however, greater from element to element in this series resulting from poor shielding by 5*f* electrons.

- **Oxidation States:** There is a greater range of oxidation states, which is in part attributed to the fact that the 5*f*, 6*d* and 7*s* levels are of comparable energies. The known oxidation states of actinoids are listed in Table 3.

Table 3. Oxidation States of Actinium and Actinoids

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3		3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4						
		5	5	5	5	5								
			6	6	6	6								
				7	7									

The actinoids show in general +3 oxidation state. The elements in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements (Table 3). The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse. Because the distribution of oxidation states among the actinoids is so uneven and so different for the former and later elements, it is unsatisfactory to review their chemistry in terms of oxidation states.

General Characteristics & Comparison with Lanthanoids:

- ***Physical State*:** The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanoids.

- ***Chemical Reactivity*:** The actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most non metals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalies have no action.

- ***Magnetic Properties*:** The magnetic properties of the actinoids are more complex than those of the lanthanoids. Although the variation in the magnetic susceptibility of the actinoids with the number of unpaired 5 *f* electrons is roughly parallel to the corresponding results for the lanthanoids, the latter have higher values.

- ***Ionisation Enthalpy*:** It is evident from the behaviour of the actinoids that the ionisation enthalpies of the early actinoids, though not accurately known, are lower than for the early lanthanoids. This is quite reasonable since it is to be expected that when 5f orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5*f* electrons, will therefore, be more effectively shielded from the nuclear charge than the 4*f* electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

- ***Actinoids vs Lanthanoids*:** A comparison of the actinoids with the lanthanoids, with respect to different characteristics as discussed above, reveals that behaviour similar to that of the lanthanoids is not evident until the second half of the actinoid series. However, even the early actinoids resemble the lanthanoids in showing close similarities with each other and in gradual variation in properties which do not entail change in oxidation state. The lanthanoid and actinoid contractions have extended effects on the sizes, and therefore, the properties of the elements succeeding them in their respective periods. The lanthanoid contraction is more important because the chemistry of elements succeeding the actinoids are much less known at the present time.

Example 1: Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

Solution: Cerium (Z = 58)

Example 2: Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

Solution: This is because of the poor shielding effect of 5f electrons in actinoids as compared to 4*f* electrons of lanthanoids.

Applications of *d*- and *f*- Block Elements

Iron and steels are the most important construction materials. Their production is based on the reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals such as Cr, Mn and Ni. Some compounds are manufactured for special purposes such as TiO for the pigment industry and MnO_2 for use in dry battery cells. The battery industry also requires Zn and Ni /Cd. The elements of Group 11 are still worthy of being called the coinage metals, although Ag and Au are restricted to collection items and the contemporary UK ‘copper’ coins are copper-coated steel. The ‘silver’ UK coins are a Cu /Ni alloy. Many of the metals and/or their compounds are essential catalysts in the chemical industry. V_2O_5 catalyses the oxidation step of SO_2 in the manufacture of sulphuric acid. $TiCl_4$ with $A1(CH_3)_3$ forms the basis of the Ziegler catalysts used to manufacture polyethylene (polythene). Iron catalysts are used in the Haber process for the production of ammonia from N_2 /H_2 mixtures. Nickel catalysts enable the hydrogenation of fats to proceed. In the Wacker process the oxidation of ethyne to ethanal is catalysed by $PdCl_2$. Nickel complexes are useful in the polymerisation of alkynes and other organic compounds such as benzene. The photographic industry relies on the special light-sensitive properties of AgBr.

Summary

In this module, we have learnt about the two series of inner transition elements, lanthanoids and actinoids which 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. The chemistry of the actinoids is more complex in view of their ability to exist in different oxidation states. Furthermore, many of the actinoid elements are radioactive which make the study of these elements rather difficult.

Also, we learned that there are many useful applications of the *d*- and *f*-block elements and their compounds, notable among them being in varieties of steels, catalysts, complexes, organic syntheses, etc.