

- (c) Oxalate ion or oxalic acid is oxidised at 333 K:  

$$5\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$$
- (d) Hydrogen sulphide is oxidised, sulphur being precipitated:  

$$\text{H}_2\text{S} \longrightarrow 2\text{H}^+ + \text{S}^{2-}$$

$$5\text{S}^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{S}$$
- (e) Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid:  

$$5\text{SO}_3^{2-} + 2\text{MnO}_4^- + 6\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 5\text{SO}_4^{2-}$$
- (f) Nitrite is oxidised to nitrate:  

$$5\text{NO}_2^- + 2\text{MnO}_4^- + 6\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 5\text{NO}_3^- + 3\text{H}_2\text{O}$$

**2.** In neutral or faintly alkaline solutions:

- (a) A notable reaction is the oxidation of iodide to iodate:  

$$2\text{MnO}_4^- + \text{H}_2\text{O} + \text{I}^- \longrightarrow 2\text{MnO}_2 + 2\text{OH}^- + \text{IO}_3^-$$
- (b) Thiosulphate is oxidised almost quantitatively to sulphate:  

$$8\text{MnO}_4^- + 3\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \longrightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + 2\text{OH}^-$$
- (c) Manganous salt is oxidised to  $\text{MnO}_2$ ; the presence of zinc sulphate or zinc oxide catalyses the oxidation:  

$$2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \longrightarrow 5\text{MnO}_2 + 4\text{H}^+$$

**Note:** Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.

*Uses:* Besides its use in analytical chemistry, potassium permanganate is used as a favourite oxidant in preparative organic chemistry. Its uses for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.

### THE INNER TRANSITION ELEMENTS (*f*-BLOCK)

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 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 8.9.

## 8.5 The Lanthanoids

### 8.5.1 Electronic Configurations

It may be noted that atoms of these elements have electronic configuration with  $6s^2$  common but with variable occupancy of  $4f$  level (Table 8.9). However, the electronic configurations of all the tripositive ions (the most stable oxidation state of all the lanthanoids) are of the form  $4f^n$  ( $n = 1$  to  $14$  with increasing atomic number).

### 8.5.2 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.

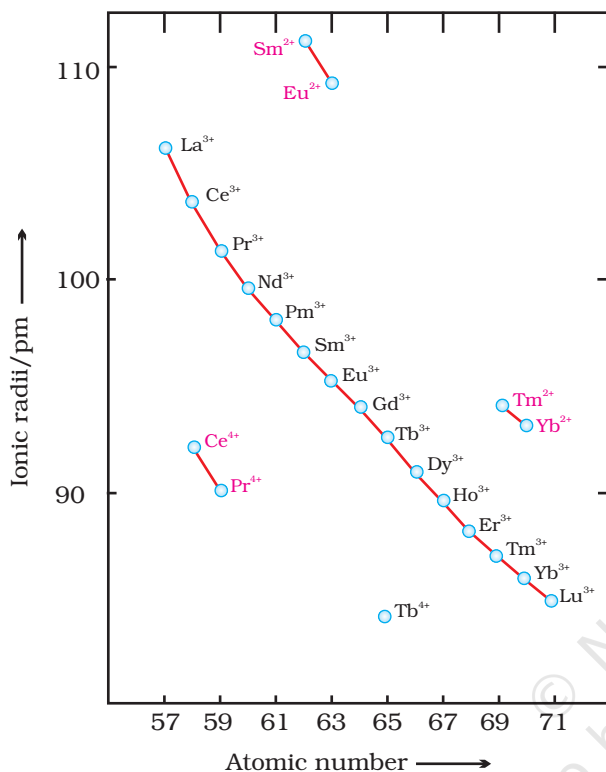


Fig. 8.6: Trends in ionic radii of lanthanoids

The decrease in atomic radii (derived from the structures of metals) is not quite regular as it is regular in  $M^{3+}$  ions (Fig. 8.6). 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 fairly regular decrease in the sizes with increasing atomic number.

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.

### 8.5.3 Oxidation States

In the lanthanoids, La(II) 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  $E^\circ$  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.

**Table 8.9: Electronic Configurations and Radii of Lanthanum and Lanthanoids**

Atomic Number	Name	Symbol	Electronic configurations*			Radii/pm		
			Ln	Ln <sup>2+</sup>	Ln <sup>3+</sup>	Ln <sup>4+</sup>	Ln	Ln <sup>3+</sup>
57	Lanthanum	La	5d <sup>1</sup> 6s <sup>2</sup>	5d <sup>1</sup>	4f <sup>0</sup>		187	106
58	Cerium	Ce	4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>2</sup>	4f <sup>1</sup>	4f <sup>0</sup>	183	103
59	Praseodymium	Pr	4f <sup>3</sup> 6s <sup>2</sup>	4f <sup>3</sup>	4f <sup>2</sup>	4f <sup>1</sup>	182	101
60	Neodymium	Nd	4f <sup>4</sup> 6s <sup>2</sup>	4f <sup>4</sup>	4f <sup>3</sup>	4f <sup>2</sup>	181	99
61	Promethium	Pm	4f <sup>5</sup> 6s <sup>2</sup>	4f <sup>5</sup>	4f <sup>4</sup>		181	98
62	Samarium	Sm	4f <sup>6</sup> 6s <sup>2</sup>	4f <sup>6</sup>	4f <sup>5</sup>		180	96
63	Europium	Eu	4f <sup>7</sup> 6s <sup>2</sup>	4f <sup>7</sup>	4f <sup>6</sup>		199	95
64	Gadolinium	Gd	4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>7</sup> 5d <sup>1</sup>	4f <sup>7</sup>		180	94
65	Terbium	Tb	4f <sup>9</sup> 6s <sup>2</sup>	4f <sup>9</sup>	4f <sup>8</sup>	4f <sup>7</sup>	178	92
66	Dysprosium	Dy	4f <sup>10</sup> 6s <sup>2</sup>	4f <sup>10</sup>	4f <sup>9</sup>	4f <sup>8</sup>	177	91
67	Holmium	Ho	4f <sup>11</sup> 6s <sup>2</sup>	4f <sup>11</sup>	4f <sup>10</sup>		176	89
68	Erbium	Er	4f <sup>12</sup> 6s <sup>2</sup>	4f <sup>12</sup>	4f <sup>11</sup>		175	88
69	Thulium	Tm	4f <sup>13</sup> 6s <sup>2</sup>	4f <sup>13</sup>	4f <sup>12</sup>		174	87
70	Ytterbium	Yb	4f <sup>14</sup> 6s <sup>2</sup>	4f <sup>14</sup>	4f <sup>13</sup>		173	86
71	Lutetium	Lu	4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>	4f <sup>14</sup> 5d <sup>1</sup>	4f <sup>14</sup>	–	–	–

\* Only electrons outside [Xe] core are indicated

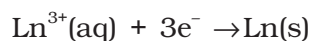
#### 8.5.4 General Characteristics

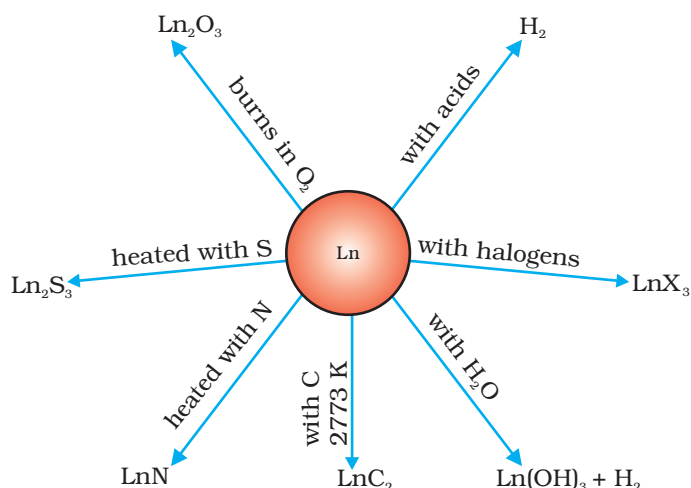
All the lanthanoids are silvery white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number, samarium being steel hard. Their melting points range between 1000 to 1200 K but samarium melts at 1623 K. They have typical metallic structure and are good conductors of 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 solutions. Colour of these ions may be attributed to the presence of *f* electrons. Neither La<sup>3+</sup> nor Lu<sup>3+</sup> 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*<sup>0</sup> type (La<sup>3+</sup> and Ce<sup>4+</sup>) and the *f*<sup>14</sup> type (Yb<sup>2+</sup> and Lu<sup>3+</sup>) are all paramagnetic.

The first ionisation enthalpies of the lanthanoids are around 600 kJ mol<sup>-1</sup>, the second about 1200 kJ mol<sup>-1</sup> 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.

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*<sup>⊖</sup> for the half-reaction:





**Fig 8.7:** Chemical reactions of the lanthanoids.

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,  $\text{Ln}_3\text{C}$ ,  $\text{Ln}_2\text{C}_3$  and  $\text{LnC}_2$  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  $\text{M}_2\text{O}_3$  and hydroxides  $\text{M}(\text{OH})_3$ . 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. 8.7.

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

## 8.6 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 8.10.

**Table 8.10: Some Properties of Actinium and Actinoids**

Atomic Number	Name	Symbol	Electronic configurations*			Radii/pm	
			M	$\text{M}^{3+}$	$\text{M}^{4+}$	$\text{M}^{3+}$	$\text{M}^{4+}$
89	Actinium	Ac	$6d^17s^2$	$5f^0$		111	
90	Thorium	Th	$6d^27s^2$	$5f^1$	$5f^0$		99
91	Protactinium	Pa	$5f^26d^17s^2$	$5f^2$	$5f^1$		96
92	Uranium	U	$5f^36d^17s^2$	$5f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^46d^17s^2$	$5f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^67s^2$	$5f^5$	$5f^4$	100	90
95	Americium	Am	$5f^77s^2$	$5f^6$	$5f^5$	99	89
96	Curium	Cm	$5f^76d^17s^2$	$5f^7$	$5f^6$	99	88
97	Berkelium	Bk	$5f^97s^2$	$5f^8$	$5f^7$	98	87
98	Californium	Cf	$5f^{10}7s^2$	$5f^9$	$5f^8$	98	86
99	Einsteinium	Es	$5f^{11}7s^2$	$5f^{10}$	$5f^9$	–	–
100	Fermium	Fm	$5f^{12}7s^2$	$5f^{11}$	$5f^{10}$	–	–
101	Mendelevium	Md	$5f^{13}7s^2$	$5f^{12}$	$5f^{11}$	–	–
102	Nobelium	No	$5f^{14}7s^2$	$5f^{13}$	$5f^{12}$	–	–
103	Lawrencium	Lr	$5f^{14}6d^17s^2$	$5f^{14}$	$5f^{13}$	–	–

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.

### 8.6.1 Electronic Configurations

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  $5f$  orbitals. Thus, the configurations of Am and Cm are  $[Rn] 5f^7 7s^2$  and  $[Rn] 5f^7 6d^1 7s^2$ . Although the  $5f$  orbitals resemble the  $4f$  orbitals in their angular part of the wave-function, they are not as buried as  $4f$  orbitals and hence  $5f$  electrons can participate in bonding to a far greater extent.

### 8.6.2 Ionic Sizes

The general trend in 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  $5f$  electrons.

### 8.6.3 Oxidation States

There is a greater range of oxidation states, which is in part attributed to the fact that the  $5f$ ,  $6d$  and  $7s$  levels are of comparable energies. The known oxidation states of actinoids are listed in Table 8.11.

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 8.11). 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.

Table 8.11: 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									

### 8.6.4 General Characteristics and Comparison with Lanthanoids

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.

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; alkalis have no action.

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  $5f$  electrons is roughly parallel to the corresponding results for the lanthanoids, the latter have higher values.

It is evident from the behaviour of the actinoids that the ionisation enthalpies of the early actinoids, though not accurately known, but 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  $5f$  electrons, will therefore, be more effectively shielded from the nuclear charge than the  $4f$  electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

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 8.10** Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

**Solution** Cerium ( $Z = 58$ )

### Intext Question

**8.10** Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

## 8.7 Some 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 of  $SO_2$  in the manufacture of sulphuric acid.  $TiCl_4$  with  $Al(CH_3)_3$  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

The **d-block** consisting of **Groups 3-12** occupies the large middle section of the **periodic table**. In these elements the inner *d* orbitals are progressively filled. The **f-block** is placed **outside** at the **bottom** of the **periodic table** and in the elements of this block, *4f* and *5f* orbitals are progressively filled.

Corresponding to the filling of *3d*, *4d* and *5d* orbitals, three series of transition elements are well recognised. All the transition elements exhibit typical metallic properties such as –high tensile strength, ductility, malleability, thermal and electrical conductivity and metallic character. Their melting and boiling points are high which are attributed to the involvement of  $(n-1)d$  electrons resulting into **strong interatomic bonding**. In many of these properties, the maxima occur at about the middle of each series which indicates that one unpaired electron per *d* orbital is particularly a favourable configuration for strong interatomic interaction.

**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. The involvement of  **$(n-1)d$  electrons** in the behaviour of transition elements impart certain distinct characteristics to these elements. Thus, in addition to variable oxidation states, they exhibit paramagnetic behaviour, catalytic properties and tendency for the formation of coloured ions, interstitial compounds and complexes.

The **transition elements** vary widely in their chemical behaviour. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble'. 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. Potassium dichromate and potassium permanganate are common examples. Potassium dichromate is prepared from the chromite ore by fusion with alkali in presence of air and acidifying the extract. Pyrolusite ore ( $MnO_2$ ) is used for the preparation of potassium permanganate. Both the dichromate and the permanganate ions are strong oxidising agents.

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