

# THE *f* BLOCK ELEMENTS. THE INNER TRANSITION ELEMENTS

The *f* block elements\* are those which have partly filled *f* subshells of the third to the outermost (antepenultimate), i.e., (*n*-2)th energy shells in their elementary or ionic state. These elements are also called inner transition elements and are divided into two series, viz.,

- (i) *The Lanthanoid Series*
- (ii) *The Actinoid Series*

In lanthanoids, it is the  $4f$  subshell which is being successively filled while in actinoids, it is the  $5f$  subshell which is being successively filled.

## THE LANTHANOID SERIES

Lanthanum ( $Z = 57$ ) and the next fourteen elements ( $Z = 58 - 71$ ) which follow it are called lanthanoids or lanthanones. These fifteen elements closely resemble one another and form a distinct group with lanthanum as the prototype ; hence the name *lanthanoids* or *lanthanones*. The reason why they resemble lanthanum so closely lies in their electronic configurations. The configuration of lanthanum is  $[Xe]5d^16s^2$ . In the succeeding fourteen elements, 14 electrons are successively added to the empty  $4f$  subshell of the lanthanum configuration. Thus, while in cerium, the element immediately following lanthanum, one  $4f$  electron is added to the lanthanum configuration, in lutetium, the last element of the series, fourteen  $4f$  electrons are added to the lanthanum configuration. Hence, the configurations of cerium and lutetium are  $[Xe]4f^15d^16s^2$  and  $[Xe]4f^{14}5d^16s^2$ , respectively. Since the number of electrons in the outermost, as well as the penultimate shell, remains the same, all the fifteen lanthanoids resemble one another very closely. Strictly speaking, only 13 elements from Ce to Yb are *f* block elements because in lanthanum ( $5d^16s^2$ ) the  $4f$  subshell is completely empty, while in lutetium ( $4f^{14}5d^15s^2$ ), the  $4f$  subshell is completely filled. However, all the elements from La to Lu have similar chemical and physical properties and hence are considered together. The reason for their similar properties is that the  $4f$  electrons in which alone they differ are embedded in the interior while  $5d$  and  $6s$  electrons which are alike are exposed more to the surroundings. This aspect will be discussed a little later in this chapter.

**Occurrence.** The lanthanoids were originally called rare earth elements. The word 'earth' was used because they occurred as oxides (which in early usage meant earth) and the word 'rare' was used because their occurrence was believed to be very scarce. Now many elements occur even more rarely than the lanthanoids. Hence, although they are not abundant by any means, they are not considered to be rare in the sense in which this word was used before. Their substantial deposits occur in several countries, particularly India, Scandinavia, U.S.A. and Russia. The most commonly occurring lanthanoid is cerium which constitutes about  $3 \times 10^{-4}$  per cent of the earth's crust. *Monazite sand* is the most important mineral containing lanthanoids. It is essentially a lanthanoid orthophosphate. Some monazite deposits contain appreciable amounts of thorium also. In some cases the concentration of thorium may amount to as much as 30 per cent.

\* According to IUPAC, the ending *ide* normally indicates a negative ion and therefore lanthanoid and actinoid are preferred to lanthanide and actinide.

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The abundance with which these elements occur in the earth's crust is shown in Table 1. The number of naturally occurring isotopes is also shown in the last column.

It is interesting to note that elements with even atomic numbers are relatively more abundant and also have a larger number of isotopes. The elements with odd atomic numbers are less abundant and do not have more than two isotopes. Promethium ( $Z = 61$ ) does not occur in nature. It has been made artificially by radioactive disintegration.

## Properties of Lanthanoids

**1. Electronic Configurations.** Electronic configurations of lanthanoids are given in Table 2. There is, however, some doubt regarding these configurations. This arises from the complexity of the electronic spectra of these elements. According to one view, the configurations are as given in column 3. According to another view, the configurations are as given in column 4. As can be seen, according to the latter view, the solitary  $5d$  electron shifts into  $4f$  subshell in all cases except in gadolinium ( $Z = 64$ ) where such a shift destroys the symmetry of a half-filled  $f$  subshell.

All the lanthanoids have been allotted one single position in the periodic table on account of the great similarity in their electronic configurations and chemical properties.

**2. Oxidation States.** The common oxidation state of all the lanthanoids is +3. Lanthanum shows +3 oxidation state through the loss of both of the  $6s$  electrons and also the solitary  $d$  electron. The configuration of  $\text{La}^{3+}$  ion, evidently, is that of xenon which is highly stable. It is very difficult, therefore, to remove another electron from this structure. Hence, a higher oxidation state for lanthanum is not possible ordinarily. In other words, it is not possible, ordinarily, to have  $\text{La}^{4+}$  ion. Similarly, gadolinium and lutetium also form only the tripositive  $M^{3+}$  ions. This is because the removal of three electrons yields the stable  $[\text{Xe}]4f^7$  configuration for  $\text{Gd}^{3+}$  ion in which the  $f$  subshell is exactly half-filled and the stable  $[\text{Xe}]4f^{14}$  configuration for  $\text{Lu}^{3+}$  ion in which the  $f$  subshell is fully filled. In these cases, therefore, any oxidation

**TABLE 1**  
**Abundance of Lanthanoids**

Element	Symbol	Atomic number	Abundance (ppm of earth's crust)	Number of naturally occurring isotopes
Lanthanum	La	57	0.7	1
Cerium	Ce	58	66	4
Praseodymium	Pr	59	9.1	1
Neodymium	Nd	60	40	7
Promethium	Pm	61	—	0
Samarium	Sm	62	7.0	7
Europium	Eu	63	2.1	2
Gadolinium	Gd	64	6.1	7
Terbium	Tb	65	1.2	1
Dysprosium	Dy	66	4.5	7
Holmium	Ho	67	1.4	1
Erbium	Er	68	3.5	6
Thulium	Tm	69	0.5	1
Ytterbium	Yb	70	3.1	7
Lutetium	Lu	71	0.8	2

complexity of the electronic spectra of these elements. According to one view, the configurations are as given in column 3. According to another view, the configurations are as given in column 4. As can be seen, according to the latter view, the solitary  $5d$  electron shifts into  $4f$  subshell in all cases except in gadolinium ( $Z = 64$ ) where such a shift destroys the symmetry of a half-filled  $f$  subshell.

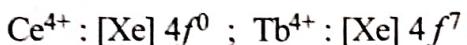
**TABLE 2**  
**Electronic Configurations and Oxidation States of Lanthanoids**

Element	Atomic Number	Electronic Configuration	Alternative Probable Configuration	Oxidation States
La	57	$[\text{Xe}] 5d^1 6s^2$	—	+3
Ce	58	$[\text{Xe}] 4f^1 5d^1 6s^2$	$[\text{Xe}] 4f^2 6s^2$	+3, +4
Pr	59	$[\text{Xe}] 4f^2 5d^1 6s^2$	$[\text{Xe}] 4f^3 6s^2$	+3, +4
Nd	60	$[\text{He}] 4f^3 5d^1 6s^2$	$[\text{Xe}] 4f^4 6s^2$	+2, +3, +4
Pm	61	$[\text{Xe}] 4f^4 5d^1 6s^2$	$[\text{Xe}] 4f^5 6s^2$	+3
Sm	62	$[\text{Xe}] 4f^5 5d^1 6s^2$	$[\text{Xe}] 4f^6 6s^2$	+2, +3
Eu	63	$[\text{Xe}] 4f^6 5d^1 6s^2$	$[\text{Xe}] 4f^7 6s^2$	+2, +3
Gd	64	$[\text{Xe}] 4f^7 5d^1 6s^2$	$[\text{Xe}] 4f^7 5d^1 6s^2$	+3
Tb	65	$[\text{Xe}] 4f^8 5d^1 6s^2$	$[\text{Xe}] 4f^9 6s^2$	+3, +4
Dy	66	$[\text{Xe}] 4f^9 5d^1 6s^2$	$[\text{Xe}] 4f^{10} 6s^2$	+3, +4
Ho	67	$[\text{Xe}] 4f^{10} 5d^1 6s^2$	$[\text{Xe}] 4f^{11} 6s^2$	+3
Er	68	$[\text{Xe}] 4f^{11} 5d^1 6s^2$	$[\text{Xe}] 4f^{12} 6s^2$	+3
Tm	69	$[\text{Xe}] 4f^{12} 5d^1 6s^2$	$[\text{Xe}] 4f^{13} 6s^2$	+2, +3
Yb	70	$[\text{Xe}] 4f^{13} 5d^1 6s^2$	$[\text{Xe}] 4f^{14} 6s^2$	+2, +3
Lu	71	$[\text{Xe}] 4f^{14} 5d^1 6s^2$	$[\text{Xe}] 4f^{14} 5d^1 6s^2$	+3

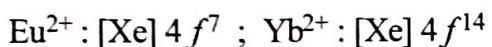
This is because the removal of three electrons yields the stable  $[\text{Xe}]4f^7$  configuration for  $\text{Gd}^{3+}$  ion in which the  $f$  subshell is exactly half-filled and the stable  $[\text{Xe}]4f^{14}$  configuration for  $\text{Lu}^{3+}$  ion in which the  $f$  subshell is fully filled. In these cases, therefore, any oxidation

state other than +3 would not occur. In other lanthanoids, other oxidation states, +2 and +4 in particular also occur. But these states are always less stable than the +3 state which is characteristic of this family. The outer electronic configurations of lanthanoids in different oxidation states are given in Table 3. The configuration of neutral atoms are also included in the table for easy reference.

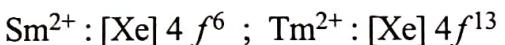
The +2 and +4 oxidation states are shown by those elements which by doing so attain the stable  $f^0$ ,  $f^7$  and  $f^{14}$  configurations. For example, cerium (Ce) and terbium (Tb) attain  $f^0$  and  $f^7$  configurations, respectively, when they go into +4 oxidation state, as shown below :



Similarly, europium and ytterbium acquire the  $f^7$  and  $f^{14}$  configurations, respectively, when they change into +2 oxidation state, as shown below :



These facts explain why these elements exercise oxidation states other than +3 as well. This argument, however, does not hold good when we find that samarium and thulium also show oxidation state of +2, even though the  $\text{M}^{2+}$  ions have  $f^6$  and  $f^{13}$  configurations, respectively :



It may be noted that  $\text{M}^+$  ions of Sm and Tm would have acquired  $f^7$  and  $f^{14}$  configurations and according to the general rule that exactly half-filled and completely filled subshells are highly stable, the +1 oxidation state of these elements should have been more stable. But, samarium and thulium do not form  $\text{M}^+$  ions at all.

Similarly, praseodymium (Pr) shows oxidation state of +4 giving  $\text{M}^{4+}$  ion with  $f^1$  configuration but does not show oxidation state of +5 although  $\text{M}^{5+}$  ion would have attained  $f^0$  (*i.e.*, empty  $f$  shell) configuration which would have been more stable. It is also seen that neodymium gives  $\text{M}^{4+}$  ion with  $f^0$  configuration and not  $\text{M}^{6+}$  ion with  $f^0$  configuration although the latter should have been more stable.

It is evident from the above discussion that although special stability associated with empty, half-filled and completely filled  $f$  subshells (*i.e.*,  $f^0$ ,  $f^7$  and  $f^{14}$  structures) is an important factor, there are some other factors which are of equal or even greater importance in determining the stabilities of the oxidation states. These factors are based on highly complicated thermodynamic and kinetic considerations which are still not quite certain.

The  $\text{M}^{4+}$  ions in aqueous solution have a tendency to change readily into  $\text{M}^{3+}$  ions. The standard potential of the reduction half-cell reaction involving reduction of  $\text{Ce}^{4+}$ , for instance, is 1.61 volt.



$$E^\circ = 1.61 \text{ volt}$$

This indicates that  $\text{Ce}^{4+}$  ion is as strong an oxidising agent as  $\text{MnO}_4^-$  ion. Other +4 lanthanoid ions like  $\text{Pr}^{4+}$  and  $\text{Tb}^{4+}$  are even more powerful oxidising agents.

**TABLE 3**  
**Outer Electronic Configurations of Lanthanoids in Different Oxidation States**

Element	Oxidation States	Outer Electronic Configuration of:			
		M	$\text{M}^{2+}$	$\text{M}^{3+}$	$\text{M}^{4+}$
La	+3	$5d^1 6s^2$	—	$5d^0 6s^0$	—
Ce	+3, +4	$4f^2 6s^2$	—	$4f^1 6s^0$	$4f^0 6s^0$
Pr	+3, +4	$4f^3 6s^2$	—	$4f^2 6s^0$	$4f^1 6s^0$
Nd	+2, +3, +4	$4f^4 6s^2$	$4f^4 6s^0$	$4f^3 6s^0$	$4f^2 6s^0$
Pm	+3	$4f^5 6s^2$	—	$4f^4 6s^0$	—
Sm	+2, +3	$4f^6 6s^2$	$4f^6 6s^0$	$4f^5 6s^0$	—
Eu	+2, +3	$4f^7 6s^2$	$4f^7 6s^0$	$4f^6 6s^0$	—
Gd	+3	$4f^7 5d^1 6s^2$	—	$4f^7 6s^0$	—
Tb	+3, +4	$4f^9 6s^2$	—	$4f^8 6s^0$	$4f^7 6s^0$
Dy	+3, +4	$4f^{10} 6s^2$	—	$4f^9 6s^0$	$4f^8 6s^0$
Ho	+3	$4f^{11} 6s^2$	—	$4f^{10} 6s^0$	—
Er	+3	$4f^{12} 6s^2$	—	$4f^{11} 6s^0$	—
Tm	+2, +3	$4f^{13} 6s^2$	$4f^{13} 6s^0$	$4f^{12} 6s^0$	—
Yb	+2, +3	$4f^{14} 6s^2$	$4f^{14} 6s^0$	$4f^{13} 6s^0$	—
Lu	+3	$4f^{14} 5d^1 6s^2$	—	$4f^{14} 6s^0$	—

**3. Ionic Radii. Lanthanoid Contraction.** The radii of  $M^{3+}$  ions, which are the most stable, are given in Table 4.

This table shows very clearly how ionic size decreases as we move along the lanthanoid series from lanthanum to lutetium. It will be seen that on going from  $La^{3+}$  to  $Lu^{3+}$ , the ionic radius shrinks from  $1\cdot15\text{ \AA}$  to  $0\cdot93\text{ \AA}$ . The steady decrease in ionic radius all along the series amounting in all to  $0\cdot22\text{ \AA}$ , is called the lanthanoid contraction.

**Consequences of Lanthanoid Contraction.** Lanthanoid contraction, as will be seen shortly, is an important factor in allowing the separation of lanthanoids from one another. Not only that ; the lanthanoid contraction has a highly significant effect on the relative properties of the elements which precede and follow the lanthanoids in the periodic table. The radius of  $La^{3+}$  ion ( $1\cdot15\text{ \AA}$ ), for example, is  $0\cdot22\text{ \AA}$  larger than that of  $Y^{3+}$  ion ( $0\cdot93\text{ \AA}$ ) which lies immediately above it in the periodic table. On that basis, if the fourteen lanthanoids had not occurred between Zr and Hf, the ionic radius of  $Hf^{4+}$  ion should have been greater than that of  $Zr^{4+}$  ion (which lies immediately above it) by about  $0\cdot2\text{ \AA}$ . But the occurrence of lanthanoid contraction of about the same order almost exactly cancels the expected increase. The result is that  $Hf^{4+}$  and  $Zr^{4+}$  ions have almost identical radii. viz.,  $0\cdot81\text{ \AA}$  and  $0\cdot80\text{ \AA}$ , respectively. Zirconium ( $Z = 40$ ) and hafnium ( $Z = 72$ ) have, therefore, almost identical chemical properties.

Similarly, as a result of lanthanoid contraction, the atomic radii of the elements which follow the lanthanoids, e.g., Hf, Ta, W, etc., are very similar to those of the elements of the previous row. This will be evident from Table 5.

TABLE 4  
Ionic Radii of Lanthanoids

Ion	Radius (Å)	Ion	Radius (Å)
$La^{3+}$	$1\cdot15$	$Tb^{3+}$	$1\cdot00$
$Ce^{3+}$	$1\cdot11$	$Dy^{3+}$	$0\cdot99$
$Pr^{3+}$	$1\cdot09$	$Ho^{3+}$	$0\cdot97$
$Nd^{3+}$	$1\cdot08$	$Er^{3+}$	$0\cdot96$
$Pm^{3+}$	$1\cdot06$	$Tm^{3+}$	$0\cdot95$
$Sm^{3+}$	$1\cdot04$	$Yb^{3+}$	$0\cdot94$
$Eu^{3+}$	—	$Lu^{3+}$	$0\cdot93$
$Gd^{3+}$	$1\cdot02$		

TABLE 5

Atomic (Covalent) Radii of Elements Preceding and Following the Lanthanoids

21	22	23	24	25	26	27	28
Sc	Ti	V	Cr	Mn	Fe	Co	Ni
1·44	1·32	1·22	1·17	1·17	1·17	1·16	1·15
39	40	41	42	43	44	45	46
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
1·62	1·45	1·34	1·29	—	1·24	1·25	1·28
57	58 to 71	72	73	74	75	76	77
La	Hf	Ta	W	Re	Os	Ir	Pt
1·69	1·44	1·34	1·30	1·28	1·26	1·26	1·28

#### 14 Lanthanoids

It is seen that the expected increase in atomic size, as we go down a group (e.g., from Sc to Y and from Y to La), disappears after the lanthanoids and the pairs of elements : Zr–Hf, Nb–Ta, Mo–W, Ru–Os, Rh–Ir, Pd–Pt have almost the same size. The properties of these pairs of elements are also very similar.

It is thus a direct consequence of lanthanoid contraction that elements of the Second and Third transition series resemble each other much more closely than do the elements of the First and Second transition series.

**Cause of Lanthanoid Contraction.** The lanthanoid contraction, although more pronounced, is similar to the contraction that was encountered in *d* block (transition) elements. The cause is also the same in both cases. As we move through the lanthanoid series,  $4f$  electrons are being added one at each step. The mutual shielding effect of  $f$  electrons is very little, being even smaller than that of  $d$  electrons. This is due to the shape of the  $f$  orbitals. The nuclear charge, however, increases by one at each step. Hence the inward pull experienced by the  $4f$  electrons increases. This causes a reduction in the size of the entire  $4f^n$  subshell. The sum of the successive reductions gives the total lanthanoid contraction.

**4. Colour.** Some of the trivalent ions of lanthanoids are coloured in the solid state as well as in aqueous solution. These colours are shown in Table 6.

The colour appears to depend upon the number of  $4f$  electrons. The colour of ions containing  $x$   $4f$  electrons is about the same as those with  $(14-x)$   $4f$  electrons. The absorption bands in the visible region of electronic spectra of rare earth ions in their compounds arise because of the absorption of light in the visible range resulting in the transition of the electrons of the ions from the lower energy  $4f$  orbitals to the higher energy  $4f$  orbitals ( $f-f$  transition). A rare earth ion thus appears to be of the colour which is complementary to the colour of the light absorbed.

A remarkable characteristic of the spectra of the tripositive lanthanoid ions is the *sharpness of the individual bands*. Many of these bands are *linelike* and become even narrower as the temperature is lowered. This is, again, due to the fact that the electrons in the  $4f$  orbitals are effectively shielded from the surroundings by the overlying electrons in the  $5s$  and  $5p$  orbitals of the rare earth ions and hence absorption bands arise merely from electronic transitions within the  $4f$  level. ( $f-f$  transitions) Such transitions are more forbidden than the  $d-d$  transitions of the transition metal ions since  $4f$  electrons of lanthanoid ions are much less affected by the ligand electrons than the electrons in the  $d$  orbitals of transition metal ions in their complexes. Therefore, the selection rules are more strictly followed for transitions in the compounds of lanthanoids than in the compounds of transition metals.

**5. Magnetic Properties.** The  $\text{La}^{3+}$ ,  $\text{Lu}^{3+}$ ,  $\text{Ce}^{4+}$  and  $\text{Yb}^{2+}$  ions which have  $4f^0$  or  $4f^{14}$  electronic configurations are *diamagnetic*. The rest of the trivalent lanthanoid ions which contain unpaired electrons in the  $4f$  orbitals are *paramagnetic*. The magnetic properties of the lanthanoids are different from those of the transition elements. In general, the magnetic moments arise from two types of motion of electron. The spin motion of electron around its own axis produces magnetic moment called *spin magnetic moment* while the orbital motion of electron around the nucleus produces magnetic moment called *orbital magnetic moment*. The observed magnetic properties of a substance are thus the result of both the spin magnetic moment and the orbital magnetic moment.

In the case of compounds of transition elements ( $d$  block elements), the  $d$  electrons of the metal ion interact strongly with the electrons of the ligands (atoms, ions or molecules) surrounding the metal ion. Due to the electric field of the ligands, the orbital motion of the electrons gets restricted and thereby the orbital magnetic moment of these electrons gets almost quenched. The magnetic moment of  $d$  block elements thus arises mainly from the contribution of spin motion of the electrons. The simple relationship based on the spin contribution of the electron, *viz.*,

$$\mu = \sqrt{n(n+2)}$$

where  $n$  is the number of unpaired electrons, roughly accounts for the magnetic properties of  $d$  block elements. However, the above relationship is not valid in the case of  $f$  block elements. In these elements the  $4f$  orbitals are well shielded from the surroundings by the overlying  $5s$  and  $5p$  subshells. As a result the electric field of the ligands surrounding the ion does not restrict the orbital motion of the electrons. The orbital contribution, which was ignored in the case of  $d$  block elements, cannot be ignored in the case of  $f$  block elements.

TABLE 6  
Colour of Lanthanoid Ions

Ion	Number of $4f$ electrons	Colour	Ion	Number of $4f$ electrons	Colour
$\text{La}^{3+}$	0	Colourless	$\text{Tb}^{3+}$	8	Pale pink
$\text{Ce}^{3+}$	1	Colourless	$\text{Dy}^{3+}$	9	Yellow
$\text{Pr}^{3+}$	2	Green	$\text{Ho}^{3+}$	10	Pale yellow
$\text{Nd}^{3+}$	3	Lilac	$\text{Er}^{3+}$	11	Pink
$\text{Pm}^{3+}$	4	Pink	$\text{Tm}^{3+}$	12	Pale green
$\text{Sm}^{3+}$	5	Yellow	$\text{Yb}^{3+}$	13	Colourless
$\text{Eu}^{3+}$	6	Pale pink	$\text{Lu}^{3+}$	14	Colourless
$\text{Gd}^{3+}$	7	Colourless			

*f* block elements. The magnetic moment in such cases is given by the relationship

$$\mu = g \sqrt{J(J+1)}$$

where  $J$  is the total angular momentum quantum number.

The magnetic moments calculated by the above expression are seen to be in good agreement (with a few exceptions) with the experimental values (Table 7).

TABLE 7  
Magnetic Moments (Theoretical and Experimental) of Tripositive Lanthanide Ions

Ion	Magnetic Moment		Ion	Magnetic Moment		Ion	Magnetic Moment	
	Experimental	Theoretical		Experimental	Theoretical		Experimental	Theoretical
La <sup>3+</sup>	0	0	Sm <sup>3+</sup>	1.4 – 1.7	0.84	Ho <sup>3+</sup>	10.4 – 10.7	10.60
Ce <sup>3+</sup>	2.3 – 2.5	2.54	Eu <sup>3+</sup>	3.3 – 3.5	0	Er <sup>3+</sup>	9.4 – 9.6	9.56
Pr <sup>3+</sup>	3.4 – 3.6	3.58	Gd <sup>3+</sup>	7.9 – 8.0	7.94	Tm <sup>3+</sup>	7.1 – 7.5	7.56
Nd <sup>3+</sup>	3.5 – 3.6	3.62	Tb <sup>3+</sup>	9.5 – 9.8	9.72	Yb <sup>3+</sup>	4.3 – 4.9	4.54
Pm <sup>3+</sup>	—	2.68	Dy <sup>3+</sup>	10.4 – 10.6	10.65	Lu <sup>3+</sup>	0	0

The experimental magnetic moments of tripositive lanthanide ions are plotted in Fig. 1 against their respective atomic numbers. La<sup>3+</sup> ion is diamagnetic ( $\mu=0$ ) because of its  $f^0$  configuration. The value increases upto Nd<sup>3+</sup> ion and then drops to 1.47 for Sm<sup>3+</sup> ion. It starts rising again, becoming maximum for Dy<sup>3+</sup> ion when it is about 11. It again starts dropping becoming zero for Lu<sup>3+</sup> ( $f^{14}$  configuration) which is diamagnetic.

6. Oxidation Potentials. The standard oxidation potentials of lanthanides for the half-cell reaction



are given in Table 8.

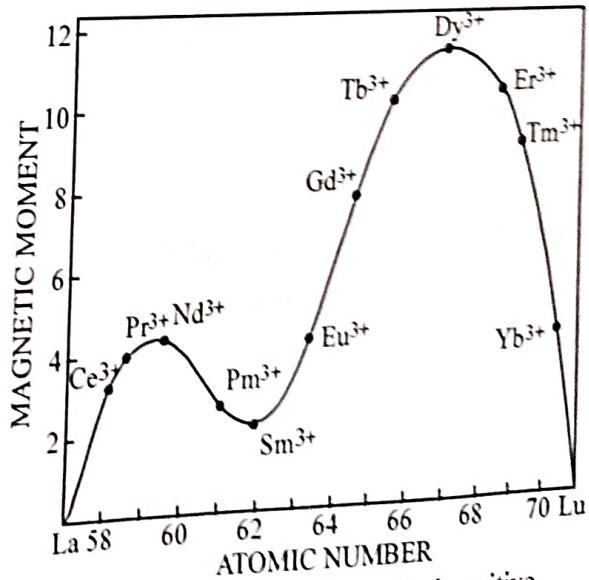


Fig. 1. Magnetic moments of tri-positive lanthanide ions.

TABLE 8  
Standard Oxidation Potentials ( $E^\circ$ )

**5. Ion Exchange Chromatography.** This is the most successful and the most rapid method for the separation of lanthanoids. We shall first explain a few terms which are used frequently in the discussion of this technique. These terms are :

**Cation exchange.** Cation exchange is a chemical reaction in which free mobile cation of a solid (called ion exchanger) is exchanged for different ions of similar charge present in solution.

**Cation exchanger.** Cation exchanger is usually an insoluble solid, organic or inorganic, which contains cationic groups capable of undergoing exchange with other ions of similar charge present in solution. It has an open network structure. The open structure permits free entry and escape of the ions present in solution.

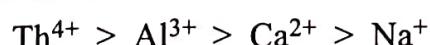
It has been well known that soils, clays and certain minerals such as zeolites, are able to exchange some of the cations they contain with other cations in solution. This property is also possessed by synthetic resins which are now widely used as ion exchangers. These are organic polymers with three-dimensional network to which ion exchange properties are imparted by attachment of ionic groups to the network. The cation exchange properties are imparted by the introduction of acid groups such as carboxylic ( $\text{COOH}$ ), sulphonic ( $\text{SO}_3\text{H}$ ) and phenolic ( $\text{OH}$ ). In these resins, the hydrogen ions are mobile and exchangeable with other cations. The anions (e.g.,  $\text{COO}^-$ ,  $\text{SO}_3^{2-}$  and  $\text{O}^{2-}$ ) remain attached to the resin network. When such a resin is placed in a solution of a salt, some of the  $\text{H}^+$  ions of the resin enter the solution and an equivalent quantity of the cations of the salt get attached to the resin. The reaction with a trivalent lanthanoid ion may be represented as



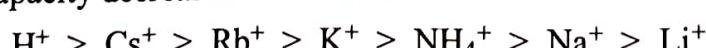
The reaction is reversible as represented above.

**Cation exchange capacity.** The capacity of an ion to undergo the exchange reaction depends upon the **charge** and the **size** of the hydrated ion in solution. Under similar conditions, the capacity increases with increase in the charge on the ion (i.e., the valency of the ion) and decreases with increase in the size of the hydrated ion.

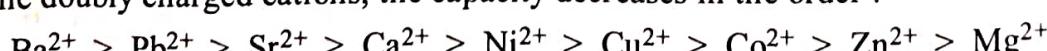
When hydrated ions of the same size are compared, it has been found that the ionic charge plays an important role in determining their capacity to undergo the exchange reactions. According to this view, the capacity amongst cations decreases in the order :



For ions carrying the same charge, the size of the hydrated ions is more important. Thus, amongst the univalent cations, the capacity decreases in the order :



Amongst the doubly charged cations, the capacity decreases in the order :



If the active ion in a resin is polyvalent and it is desired to exchange it by an ion of lower valency, the exchange is favoured invariably by using much higher concentration of the solution.

**11. Complexes.** Lanthanoid ions, in spite of the high charge (+3), have low charge density because of their large size. They cannot, therefore, cause much polarization and, consequently, they have only a weak tendency to form complexes. Their complexes with unidentate ligands are very few. However, complexes with a few chelating ligands such as  $\beta$ -diketones, oximes and ethylenediaminetetraacetic acid (EDTA) are fairly common. The lanthanoids do not form complexes with  $\pi$  bonding ligands such as CO, NO, CNR, etc. The tendency to form complexes and their stability increases with increasing atomic number. Advantage is taken of this fact in their separation from one another.

**Electronic Configurations.** There is some uncertainty with regard to outer electronic configurations of these elements. There is doubt whether thorium, protactinium and uranium contain any  $5f$  electrons at all. It has been suggested that in these elements the additional electrons enter the  $6d$  subshell and not  $5f$  subshell and that the entry into the  $5f$  subshell begins only after uranium. According to this suggestion, the elements following uranium, in which the  $5f$  subshell is definitely being filled, are called **urenides**. The uncertainty with respect to the entry of electrons in  $5f$  or  $6d$  subshell is due to the fact that both these subshells are of almost equal energy. Not only this ; the nuclei of these elements are also unstable and

undergo radioactive decay. In some cases, the determinations have been extremely difficult on account of only minute amounts of the elements that could be obtained for experimental purposes.

The probable electronic configurations of these elements, accepting the view that entry into  $5f$  subshell begins with actinium, are given in Table 9. The general electronic configuration may be written as  $[Rn]5f^{1-14}6d^{0-1}7s^2$ . These configurations are even less certain than those given for the lanthanides in Table 2. The important oxidation states of the elements are also included in the table.

TABLE 9  
Probable Electronic Configurations and Oxidation States of Actinides

Element	Symbol	Atomic number	Electronic configurations	Oxidation states*
Actinium	Ac	89	$[Rn] 6d^1 7s^1$	
Thorium	Th	90	$[Rn] 5f^1 6d^1 7s^2$	(+2), +3, (+4)
Protactinium	Pa	91	$[Rn] 5f^2 6d^1 7s^2$	(+3), +4, (+5)
Uranium	U	92	$[Rn] 5f^3 6d^1 7s^2$	(+3), +4, +5, +6
Neptunium	Np	93	$[Rn] 5f^4 6d^1 7s^2$	+3, +4, +5, +6
Plutonium	Pu	94	$[Rn] 5f^5 6d^1 7s^2$	+3, +4, +5, +6 +7
Americium	Am	95	$[Rn] 5f^6 6d^1 7s^2$	+3, +4, +5, +6 +7
Curium	Cm	96	$[Rn] 5f^7 6d^0 7s^2$	+3, (+4),
Berkeylium	Bk	97	$[Rn] 5f^7 6d^1 7s^2$	+3, (+4)
Californium	Cf	98	$[Rn] 5f^8 6d^1 7s^2$	+3, +4
Einsteinium	Es	99	$[Rn] 5f^{10} 6d^0 7s^2$	+3
Fermium	Fm	100	$[Rn] 5f^{11} 6d^0 7s^2$	+3
Mendelevium	Md	101	$[Rn] 5f^{12} 6d^0 7s^2$	+3
Nobelium	No	102	$[Rn] 5f^{13} 6d^0 7s^2$	+3
Lawrencium	Lr	103	$[Rn] 5f^{14} 6d^0 7s^2$	+2 $\frac{+3}{-3}$
			$[Rn] 5f^{14} 6d^1 7s^2$	$\pm 3$

\* Less stable oxidation states are given in brackets.

**Properties.** All these elements are radioactive and are  $\alpha$ -ray emitters. Thorium and uranium have sufficiently long half-life periods ( $1.39 \times 10^{10}$  years for  $^{232}\text{Th}$  and  $4.50 \times 10^9$  years for  $^{238}\text{U}$ ) and this is the reason why they have been occurring in nature all the time. The half-life periods of the rest of the elements are shorter than the age of the earth ( $25 \times 10^9$  years). Hence, the transuranic elements (*i.e.*, urendides) do not occur in nature and have been prepared by artificial means using nuclear reactors. However, neptunium and plutonium have been isolated in traces from uranium minerals.

Some physical constants of the first seven members of the actinide series are given in Table 10.

All the known actinides are silvery-white metals which are highly electropositive and reactive. They tarnish rapidly in air due to the formation of coating of oxides. Finely divided thorium burns spontaneously in air. The actinides react with most non-metals especially when heated.

They resist the attack of alkalies and are also less reactive towards acids. They form compounds which in aqueous solution give simple trivalent ions (hydrated) such as  $\text{Ac}^{3+}$ ,  $\text{U}^{3+}$ ,  $\text{Np}^{3+}$ ,  $\text{Pu}^{3+}$ ,  $\text{Am}^{3+}$ , etc. In this respect, the actinide elements resemble the lanthanide elements. The ions of actinide elements are paramagnetic like those of the lanthanides.

All the actinides, except thorium and americium, have high densities. They exhibit isomorphism.

TABLE 10  
Some Physical Constants of Actinides

Element	Melting point (°C)	Boiling point (°C)	Heat of vaporisation (kJ mol <sup>-1</sup> )	Density at 25°C (g ml <sup>-1</sup> )
Actinium	1050	—	293	—
Thorium	1750	3000–4200	544–740	11.72
Protactinium	1875	—	—	15.35
Uranium	1132	3818	—	19.04
Neptunium	640	—	—	20.45
Plutonium	639.5	3235	—	19.74
Americium	850–1200	2607	—	11.87

**Oxidation States.** Actinides exhibit oxidation states of +2, +3, +4, +5 and +6. The +2 state is shown only by actinium and thorium in a few compounds, e.g.,  $\text{ThBr}_2$ ,  $\text{ThI}_2$ ,  $\text{ThO}$  and  $\text{ThS}$ . The +3 oxidation state is most common (as in lanthanides). This state is shown by all the actinide elements. The +3 oxidation state becomes more and more stable with increase in atomic number. The +4 oxidation state is shown by the first 8 elements (Ac to Cm) only. The +5 oxidation state is shown by five elements from Th to Pu whereas the +6 oxidation state is exhibited only by four elements (Pa to Pu).

The various oxidation states exhibited by the actinides are reproduced in Table 11.

TABLE 11  
Oxidation States Exhibited by Actinides

Element	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Er	Fm	Md
At. No.	89	90	91	92	93	94	95	96	97	98	99	100	101
Oxidation States	+2	+2											
	+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	+5							
	+6	+6	+6	+6	+6	+6							

**Ionic Radii of Actinide Elements.** The ionic radii of the actinide elements decrease gradually as we move along the actinide series (Table 12). Thus, on going from  $\text{Ac}^{3+}$  to  $\text{Cm}^{3+}$  ion, the ionic radius decreases from 1.11 to 0.98 Å. There is also a steady decrease in the radii of  $\text{An}^{4+}$  ions ( $\text{An}$  = actinide). This steady decrease in the ionic radii with increase in the positive charge of the nucleus is called **actinide contraction** and is analogous to lanthanide contraction. This contraction in ionic radii of  $\text{An}^{3+}$  and  $\text{An}^{4+}$  ions may be attributed to the addition of successive electrons to an inner  $f$  subshell (i.e.,  $5f$ ). Thus, at each step, the nuclear charge (i.e., atomic number) increases which is not compensated due to poor shielding effect of the  $5f$  electrons. Hence, as the atomic number increases, the inward pull experienced by the  $5f$  electrons increases. Consequently, steady decrease in ionic radii occurs in actinide series.

TABLE 12  
Ionic Radii of Actinides

Element	Atomic number	Ionic radius	
		$\text{An}^{3+}$ (Å)	$\text{An}^{4+}$ (Å)
Ac	89	1.11	0.99
Th	90	1.08	0.96
Pa	91	1.05	0.93
U	92	1.03	0.92
Np	93	1.01	0.92
Pu	94	1.00	0.90
Am	95	0.99	0.89
Cm	96	0.98	0.88

**Colours of Ions.** Actinide ions are generally coloured. The appearance of colour depends upon the number of  $5f$  electrons. The ions without  $5f$  electrons (i.e., fully filled  $5d$  subshell and no  $5f$  subshell) or seven  $5f$  electrons (exactly half-filled  $f$  subshell) are colourless, as expected. The ions containing 2 to 6 electrons in the  $5f$  subshell are coloured (Table 13). The colours arise out of electronic transitions between various energy states within the  $5f$  subshell ( $f-f$  transitions).

TABLE 13

Colours of Actinide Ions in Aqueous Solutions

Ion	Number of $5f$ electrons	Colour
$\text{Ac}^{3+}$	0	colourless
$\text{U}^{3+}$	3	red
$\text{Np}^{3+}$	4	blue
$\text{Pu}^{3+}$	5	violet
$\text{Am}^{3+}$	6	pink
$\text{Cm}^{3+}$	7	colourless
$\text{Th}^{4+}$	0	colourless
$\text{U}^{4+}$	2	green
$\text{Np}^{4+}$	3	yellowish-green
$\text{Pu}^{4+}$	4	yellowish-brown
$\text{Am}^{4+}$	5	pink
$\text{Cm}^{4+}$	6	pale yellow

Actinides can also form complexes with  $\pi$  bonding ligands such as alkyl phosphines, thioethers, etc.

**Comparison with Lanthanides.** Since in actinides also, the  $f$  subshell is being filled, hence these are also called  $f$  block elements, like the lanthanides. The two series of elements have a close relationship with each other. There are a number of notable