

Group-8: Unit-3. General Chemistry of f-block elements

→ What are f-block elements/Inner transition elements?

Those elements in which last or differentiating electron enters in antepenultimate, i.e. (n-2) f-orbitals are called f-block elements. These elements are also known as inner-transition elements due to last electrons in them enters into (n-2) f-orbitals, i.e. inner to the penultimate energy level. They have ele. Conf. [Noble gas] (n-2) f<sup>1-14</sup> (n-1) d<sup>0,1</sup> ns<sup>2</sup> (where n=6 or 7)

These are elements of Group-3 and shown in two series/horizontal positions below main part of Periodic table. f-block elements are of two series: (i) 4f series/Lanthanides: Ce<sub>58</sub> to Lu<sub>71</sub>  
(ii) 5f series/Actinides: Th<sub>90</sub> to Lr<sub>103</sub>

→ What are Lanthanides?

Those elements in which last electron enters in 4f-orbitals are called 4f or first inner transition series. 4f series elements are called Lanthanides or Lanthanones since they follow lanthanum (La<sub>57</sub>). They are also called rare earths as found in earth crust in very small amounts. Outer ele. Conf. of lanthanides is 4f<sup>1-14</sup> 5d<sup>0,1</sup> 6s<sup>2</sup>. These are elements of Group-3, Period-6 (shown in 1st horizontal row below main part of P.T). They are Ce<sub>58</sub> to Lu<sub>71</sub>.

1. Electronic Configuration: General ele. Conf. of Lanthanides is [Xe]<sub>54</sub> 4f<sup>1-14</sup> 5d<sup>0,1</sup> 6s<sup>2</sup>.

In lanthanides, 4f orbitals/subshell gradually filled. Since the energies associated with 4f & 5d subshells are very close, there are some doubts regarding their ele. Conf. because the electrons can exchange their positions. The commonly accepted ele. Conf. of lanthanides are given in Table-1.

Table-1

Element	Symbol	At. No.	Ele. Conf.	Oxidation States
Cerium	Ce	58	[Xe] 4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>	+3, +4
Praseodymium	Pr	59	[Xe] 4f <sup>3</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+3, +4
Neodymium	Nd	60	[Xe] 4f <sup>4</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+2, +3, +4
Promethium	Pm	61	[Xe] 4f <sup>5</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+3
Samarium	Sm	62	[Xe] 4f <sup>6</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+2, +3
Europium	Eu	63	[Xe] 4f <sup>7</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+2, +3
Gadolinium	Gd	64	[Xe] 4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	+3
Terbium	Tb	65	[Xe] 4f <sup>9</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+3, +4
Dysprosium	Dy	66	[Xe] 4f <sup>10</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+3, +4
Holmium	Ho	67	[Xe] 4f <sup>11</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+3
Erbium	Er	68	[Xe] 4f <sup>12</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+3
Thulium	Tm	69	[Xe] 4f <sup>13</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+2, +3
Ytterbium	Yb	70	[Xe] 4f <sup>14</sup> 5d <sup>0</sup> 6s <sup>2</sup>	+2, +3
Lutetium	Lu	71	[Xe] 4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>	+3

It is clear from table that (i) Lu<sub>71</sub> has completely filled f-subshell while others are incomplete f<sub>conf</sub>. (ii) Ce<sub>58</sub>, Gd<sub>64</sub> & Lu<sub>71</sub> have single electron in d-subshell (i.e., d<sup>1</sup> conf.) (iii) Lanthanides (Eu<sub>63</sub>, Yb<sub>70</sub>) are relatively more stable since they are either half filled or completely filled f-subshell.

2. Oxidation states: Lanthanides show variable oxidation states. Oxidation states exhibited by Lanthanides are shown in Table-1. From table, it is evident that (i) the most common & stable oxidation state of lanthanides (Nd, Sm, Eu, Yb, Lu) is +3. (ii) Some lanthanides occasionally exhibit oxidation state +2 also (iii) Some lanthanides (Ce, Pr, Tb) occasionally exhibit O.S. +4 also. Sm<sup>2+</sup>, Eu<sup>2+</sup>, Tm<sup>2+</sup> & Yb<sup>2+</sup> exist in aqueous solution. Ce<sup>4+</sup>, Pr<sup>4+</sup>, Nd<sup>4+</sup>, Tb<sup>4+</sup> & Dy<sup>4+</sup> (only oxide) exist in aqueous solution. Lanthanides in O. state +2 act as reducing agent while O. state +4 act as oxidising agent.



3. Atomic & Ionic radii (Lanthanide Contraction): The atomic & ionic radii in Lanthanides show a regular change (decrease) in the size of atoms/ions with the increase in atomic number. The regular (steady) decrease in the size of Lanthanide atoms/ions with the increase in atomic number (i.e.,  $\text{La}_{57}$  to  $\text{Lu}_{71}$ ) is known as Lanthanide Contraction.

Table-2

Element	$\text{La}_{57}$	$\text{Ce}_{58}$	$\text{Pr}_{59}$	$\text{Nd}_{60}$	$\text{Pm}_{61}$	$\text{Sm}_{62}$	$\text{Eu}_{63}$	$\text{Gd}_{64}$	$\text{Tb}_{65}$	$\text{Dy}_{66}$	$\text{Ho}_{67}$	$\text{Er}_{68}$	$\text{Tm}_{69}$	$\text{Yb}_{70}$	$\text{Lu}_{71}$
Atomic radius (Å)	187	183	182	181	181	180	199	180	178	177	176	175	174	173	172
Ionic ( $\text{Ln}^{3+}$ ) radius (Å)	106	103	101	100	98	96	95	94	92	91	89	88	87	86	85

Cause of Lanthanide Contraction: Lanthanide contraction, i.e. decrease in size (atomic/ionic) from La to Lu, is due to poor shielding effect of antepenultimate, i.e.  $(n-2)$  f orbitals. On moving along Lanthanide series, the nuclear charge increases due to increase in number of protons as well as one electron increases in  $(n-2)$  f-orbital. The shielding effect is poor in case of  $(n-2)$  f orbital (order of shielding effect:  $s > p > d > f$ ) as well as it becomes very less effective if shielding is by f orbitals as they are more diffused. Evidently, the increase in nuclear charge (no. of proton) with increase in atomic number predominates over decrease in nuclear charge due to shielding effect & thus valence or outermost shells are pulled more effectively towards nucleus to show decrease in atomic/ionic size.

Consequences of Lanthanide Contraction: Some of the important consequences/effects of Lanthanide contraction are -

- (i) In Lanthanide contraction ( $\text{La}^{3+}$  to  $\text{Lu}^{3+}$ ) average decrease in atomic size is about 14 pm, which is responsible for a small decrease in electronegativity and standard oxidation potential along the series (La to Lu). So Lanthanides are chemically similar in properties.
- (ii) The basic character of oxides and hydroxides decreases from  $\text{La}_2\text{O}_3$  to  $\text{Lu}_2\text{O}_3$  /  $\text{La}(\text{OH})_3$  to  $\text{Lu}(\text{OH})_3$ . Due to smaller size of Lu, the Lu-OH bond acquires more covalent character.
- (iii) Lanthanides have similar chemical properties and it is therefore difficult to separate from each other, but ability to form complexes varies slightly which helps in their separation by ion-exchange method.
- (iv) The closer values of atomic radii for Zr-Hf, Nb-Ta & Mo-W pairs of elements of fourth and fifth d-series of a subsequent group. Here increase in size down group is cancelled by decrease in size due to Lanthanide contraction. This is the reason that members of 4d & 5d series of a group resemble more closely in comparison to 3d members.

Table-3

Group →	4	5	6
3d-series	Ti (132 pm)	V (122 pm)	Cr (130 pm)
4d-series	Zr (160 pm)	Nb (146 pm)	Mo (139 pm)
5d-series	Hf (159 pm)	Ta (146 pm)	W (140 pm)

4. Magnetic properties: We know that magnetic behaviour in <sup>chemical</sup> substances arises due to the presence of



Properties of inner transition (f-block) elements

We know that magnetic behaviour in chemical substances arises due to the presence of unpaired electrons. An electron may be regarded as an elementary or tiny magnetic. The origin of magnetism is most easily described in pre-wave mechanical terms where we make picture the electron as negatively charged particle, possesses both spinning motion on its axis and revolving motion about a nucleus. The former motion gives rise to spin moment and the later to orbital moment. The combination of these two moments results in the paramagnetic moment (i.e., paramagnetism) for certain atom/ion.

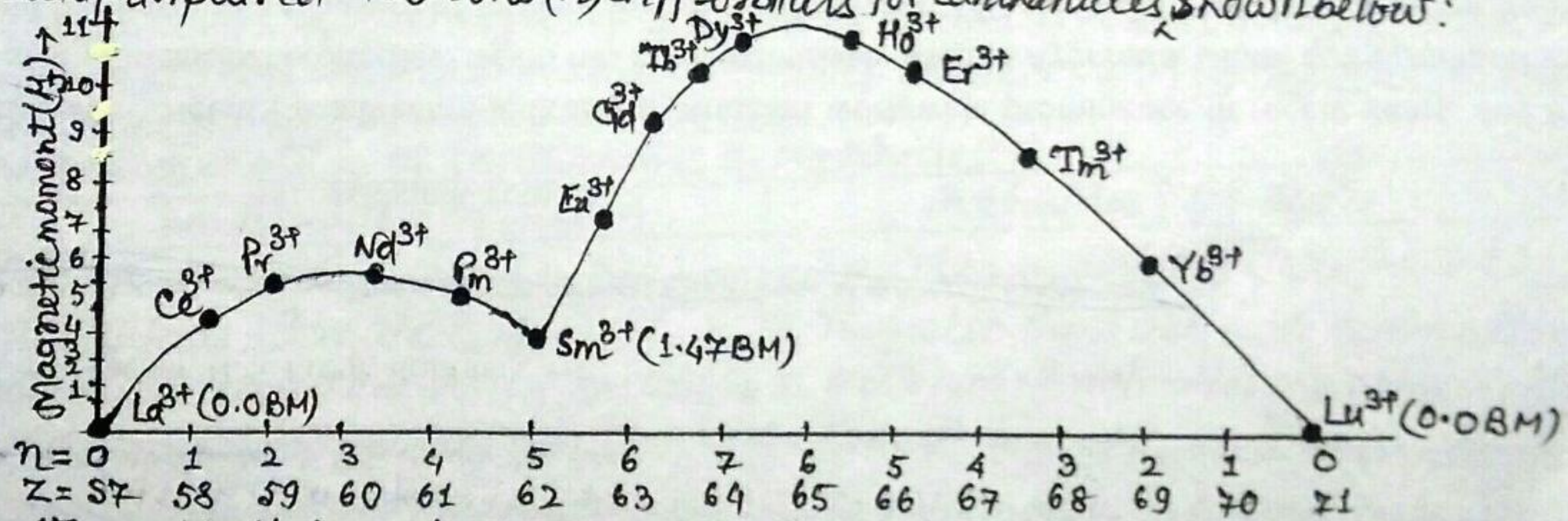
In the 4f-series (i.e., Lanthanides),  $La^{3+}$  ion is empty (i.e.,  $4f^0$  conf.) and  $Lu^{3+}$  is completely filled (i.e.,  $4f^{14}$  conf.). These ions are diamagnetic as there is no unpaired electron. The remaining  $M^{3+}$  ( $4f^1 - f^{13}$  conf.) ions are paramagnetic, since they are partly filled, i.e., presence of one or more unpaired electrons.

The magnetic behaviour of the f-block elements (Lanthanides/Actinides) is fundamentally different from that of d-block elements (transition metals). The reason for the difference is that the electrons responsible for the properties of the  $M^{3+}$  ions are 4f or 5f orbital which are effectively shielded from the influence of external forces by overlain s & p-orbitals. Due to this, it is not possible to explain the magnetic moment in term of unpaired electron atom. The orbital contribution which is ignore in the case of d-block elements, cannot be ignored in the case of f-block elements.

The simple relation for calculating magnetic moment is given by  $\mu = \sqrt{n(n+2)} BM$  (where  $n =$  no. of unpaired electrons) cannot be valid in f block elements. In the case of f block elements, the total paramagnetism is due to both spin ( $S$ ) & Orbital moments ( $L$ ), given as  $\mu_{eff} = g \sqrt{J(J+1)} BM$  (where  $g =$  a constant, called Lande Splitting factor  $= 1.5 + \frac{S(S+1) - L(L+1)}{2J(J+1)}$ ;  $J =$  total or resultant angular momentum).  $\mu_J$  values of  $M^{3+}$  ions calculated from above formula, e.g., for  $Ce^{3+}$  ( $4f^1$  conf.) ground state term is  $^2F_{5/2}$ .  $S = 1/2, L = 3, J = 5/2, g = 6/7$

$\mu_J$  or  $\mu_{eff} = g \sqrt{J(J+1)} BM = \frac{6}{7} \sqrt{5/2(5/2+1)} = 2.54 BM$ . Experimental value lie in the range 2.3-2.5 BM.

The experimental values of  $\mu_J$  (in BM) of  $M^{3+}$  ions are plotted against their atomic nos./ number of unpaired electrons ( $n$ ) in f-orbitals for Lanthanides as shown below:



From the graph, it is evident that  $La^{3+}$  ( $4f^0$ ) &  $Lu^{3+}$  ( $4f^{14}$ ) are diamagnetic ( $\mu_J = 0$ ).  $\mu_J$  values increase upto  $Nd^{3+}$  and then decrease to  $Sm^{3+}$  ion. It starts rising again and becomes maximum at  $Dy^{3+}$  (10.5 BM), and then decreases to  $Lu^{3+}$  (0.0 BM).

In actinides (5f-series), 5f-orbitals are not completely shielded from external ligand field due to their greater spatial extension. Thus, 5f electrons in actinides are more exposed to crystal field and are less effectively shielded. As a result, the orbital contribution to magnetic moment is quenched in actinides. Magnetic moment values of tri positive actinides ( $M^{3+}$ ) ions decrease from  $U^{3+}$  ( $5f^3, n=3$ ) to give minimum value at  $Pu^{3+}$  ( $5f^5, n=5$ ) and then increase to show a maximum value at  $Cf^{3+}$  ( $5f^9, n=5$ ). Thereafter it decreases at  $Es^{3+}$  ( $5f^{10}, n=4$ ).



⇒ What are Actinides?

Those elements in which the last electron enters in 5f orbitals are called 5f or second inner transition series. They are called actinides or actinones since they follow Actinium ( $Ac_{89}$ ). Outer ele. Conf. is  $5f^{1-14} 6d^0 \text{ or } 1 7s^2$ . These are elements of Group 3 and Period-7 (shown in 2nd horizontal row below main part of PT). They include 14 elements from  $Th_{90}$  to  $Lr_{103}$ . They are radioactive elements. First three elements ( $Th_{90}$ ,  $Pa_{91}$ , &  $U_{92}$ ) are natural and last 11 elements ( $Np_{93}$  to  $Lr_{103}$ ) are artificial (man made), called transuranic elements.

1. Electronic Configuration: The general electronic Conf. of actinides is  $[Rn] 5f^{1-14} 6d^0 \text{ or } 1 7s^2$ . From  $Th_{90}$  onward 5f-subshell gets progressively filled. However, there are some doubts regarding the filling of 5f & 6d subshells due to their comparable energies. The commonly accepted ele. Conf. of actinides are given in the table-4.

Table-4

Element	Symbol	At. No.	Electronic Conf.	Oxidation states
Thorium	Th	90	$[Rn] 5f^1 6d^1 7s^2$	(+3), +4
Protoactinium	Pa	91	$[Rn] 5f^2 6d^1 7s^2$	(+3), (+4), +5, (+2)
Uranium	U	92	$[Rn] 5f^3 6d^1 7s^2$	+3, +4, +5, +6, +7
Neptunium	Np	93	$[Rn] 5f^4 6d^1 7s^2$	+3, +4, +5, +6
Plutonium	Pu	94	$[Rn] 5f^6 6d^0 7s^2$	+3, (+4), +5, +6
* Americium	Am	95	$[Rn] 5f^7 6d^0 7s^2$	+3, (+4)
Curium	Cm	96	$[Rn] 5f^7 6d^1 7s^2$	+3, +4
Berkelium	Bk	97	$[Rn] 5f^9 6d^0 7s^2$	+3
Californium	Cf	98	$[Rn] 5f^{10} 6d^0 7s^2$	+3
Einsteinium	Es	99	$[Rn] 5f^{11} 6d^0 7s^2$	+3
Fermium	Fm	100	$[Rn] 5f^{12} 6d^0 7s^2$	+3
Mendelevium	Md	101	$[Rn] 5f^{13} 6d^0 7s^2$	+3
* Nobelium	No	102	$[Rn] 5f^{14} 6d^0 7s^2$	+2, +3
Lawrencium	Lr	103	$[Rn] 5f^{14} 6d^1 7s^2$	+3

2. Oxidation states: Actinides generally show variable O. states from +2 to +7 (Table-4). This is due to comparable energies of 5f, 6d & 7s subshells. The common O. state is +3. The elements in first half of the series show higher O. states. O. states of  $f^0, f^7, f^{14}$  conf. are relatively most stable. Oxidation states shown by ( ) are less stable.

⇒ Comparative study of Lanthanides & Actinides:

Lanthanides (4f-series)	Actinides (5f-series)
1. They show variable O. states (+2 to +4).	1. They show variable O. states (+2 to +7)
2. They show lanthanide contraction.	2. They also show actinide contraction (some)
3. Most ions of lanthanides ( $Ln^{3+}$ ) are coloured.	3. Most ions of actinides are coloured (due to f-f trans).
4. These are referred as rare earths.	4. Elements beyond $U_{92}$ are called transuranic elements.
5. They are natural & non-radioactive. Pm is a radioactive element.	5. They are mostly artificial. $Th, Pa, U$ are radioactive.
6. Their oxides, hydroxides are less basic in nature.	6. Their oxides, hydroxides are more basic in nature.
7. They do not form oxo-cations.	7. They form oxo-cations, e.g. $UO_2^{2+}$ .
8. They show ion-exchange behaviour & so they are separated by ion-exchange method.	8. They also show ion-exchange behaviour.
9. Their mag. prop. (Paramagnetism) can be easily explained.	9. Their mag. prop. cannot be easily explained.
10. Their physical & chem. properties have been thoroughly studied.	10. Physical & chemical properties beyond $U_{92}$ have not been studied thoroughly.