

## Lanthanides and Actinides.

Lanthanides and actinides are collectively called f-block elements because last electron in them enters into f- orbitals of the antepenultimate (i.e., inner to penultimate) shell partly but incompletely filled in their elementary or ionic states. The name inner transition, elements is also given to them because they constitute transition series with in transition series (d-block elements) and the last electron enters into antepenultimate shell (n-2) f. In addition to incomplete d-subshell, their f-subshell is also incomplete. Thus, these elements have three incomplete outer shells i.e., (n-2), (n-1) and n shells and the general electronic configuration of f-block elements is

$$(n-2) f^{1-14} (n-1) d^{0-10} ns^2.$$

**(1) Lanthanides:** The elements with atomic numbers 58 to 71 i.e. cerium to lutetium (which come immediately after lanthanum  $Z = 57$ ) are called lanthanides or lanthanones or rare earths. These elements involve the filling of 4 f-orbitals. Their general electronic configuration is,  $[Xe]4f^{1-14} 5d^{0-10} 6s^2$ . Promethium (Pm), atomic number 61 is the only synthetic (manmade) radioactive lanthanide.

Properties of lanthanides

- (i) These are highly dense metals and possess high melting points.
- (ii) They form alloys easily with other metals especially iron. e.g. misch metal consists of a rare earth element (94–95%), iron (up to 5%) and traces of S, C, Ca and Al, pyrophoric alloys contain Ce (40–5%), La + neodymium (44%), Fe (4–5%), Al (0–5%) and the rest is Ca, Si and C. It is used in the preparation of ignition devices e.g., trace bullets and shells and flints for lighters.
- (iii) Oxidation state: Most stable oxidation state of lanthanides is + 3. Oxidation states + 2 and + 4 also exist but they revert to + 3 e.g.  $Sm^{2+}$ ,  $Eu^{2+}$ ,  $Yb^{2+}$  lose electron to become + 3 and hence are good reducing agents, whereas  $Ce^{4+}$ ,  $Pr^{4+}$ ,  $Tb^{4+}$  in aqueous solution gain electron to become + 3 and hence are good oxidizing agents. There is a large gap in energy of 4 f and 5 d subshells and thus the number of oxidation states is limited.
- (iv) Color: Most of the trivalent lanthanide ions are colored both in the solid state and in aqueous solution. This is due to the partly filled f-orbitals which permit f–f transition. The elements with x f electrons have a similar color to those of  $(14 - x)$  electrons.

(v) Magnetic properties: All lanthanide ions with the exception of  $\text{Lu}^{3+}$ ,  $\text{Yb}^{3+}$  and  $\text{Ce}^{4+}$  are paramagnetic because they contain unpaired electrons in the 4 f orbitals. These elements differ from the transition elements in that their magnetic moments do not obey the simple "spin only" formula  $\mu_{\text{eff}} = \sqrt{n(n+2)}$

B.M. where n is equal to the number of unpaired electrons. In transition elements, the orbital contribution of the electron towards magnetic moment is usually quenched by interaction with electric fields of the environment but in case of lanthanides the 4 f-orbitals lie too deep in the atom for such quenching to occur. Therefore, magnetic moments of lanthanides are calculated by taking into consideration spin as well as orbital contributions and a more complex formula

$$\mu_{\text{eff}} = \sqrt{4S(S+1) + L(L+1)} \text{ B.M.}$$

Which involves the orbital quantum number L and spin quantum number S.

(vi) Complexformation: Although the lanthanide ions have a high charge (+3) yet the size of their ions is very large yielding small charge to size ratio i.e., low charge density. As a consequence, they have poor tendency to form complexes. They form complexes mainly with strong chelating agents such as EDTA,  $\beta$ -diketones, oxine etc. No complexes with  $\pi$ -bonding ligands are known.

(vii) Lanthanide contraction: The regular decrease in the size of lanthanide ions from  $\text{La}^{3+}$  to  $\text{Lu}^{3+}$  is known as lanthanide contraction. It is due to greater effect of the increased nuclear charge than that of the screening effect.

Consequences of lanthanide contraction

(a) It results in slight variation in their chemical properties which helps in their separation by ion exchange

(b) Each element beyond lanthanum has same atomic radius as that of the element lying above it in the group (e.g. Zr 145 pm, Hf 144 pm); Nb 134 pm, Ta 134 pm; Mo 129 pm, W 130 pm).



- (c) The covalent character of hydroxides of lanthanides increases as the size decreases from  $La^{3+}$  to  $Lu^{3+}$ . However basic strength decreases. Thus  $La(OH)_3$  is most basic whereas  $Lu(OH)_3$  is least basic. Similarly, the basicity of oxides also decreases in the order from  $La^{3+}$  to  $Lu^{3+}$ .
- (d) Tendency to form stable complexes from  $La^{3+}$  to  $Lu^{3+}$  increases as the size decreases in that order.
- (e) There is a slight increase in electronegativity of the trivalent ions from La to Lu.
- (f) Since the radius of  $Yb^{3+}$  ion (86 pm) is comparable to the heavier lanthanides Tb, Dy, Ho and Er, therefore they occur together in natural minerals.

**(2) Actinides:** The elements with atomic numbers 90 to 103 i.e. thorium to lawrencium (which come immediately after actinium,  $Z = 89$ ) are called actinides or actinones. These elements involve the filling of 5 f-orbitals. Their general electronic configuration is,  $[Rn]5f^{1-14}6d^{0-1}7s^2$ .

They include three naturally occurring elements thorium, protactinium and uranium and eleven transuranium elements or transuranics which are produced artificially by nuclear reactions. They are synthetic or manmade elements. All actinides are radioactive.

Properties of actinides

(i) Oxidation state: The dominant oxidation state of actinides is +3 which shows increasing stability for the heavier elements. Np shows +7 oxidation state but this is oxidizing and is reduced to the most stable state +5. Pu also shows states up to +7 and Am up to +6 but the most stable state drops to Pu (+4) and Am (+3). Bk in +4 state is strongly oxidizing but is more stable than Cm and Am in 4 state due to  $f^7$  configuration. Similarly, No is markedly stable in +2 state due to its  $f^{14}$  configuration. When the oxidation number increases to + 6, the actinide ions are no longer simple. The high charge density causes the formation of oxygenated ions e.g.,  $UO_2^{2+}$ ,  $NpO_2^{2+}$  etc. The exhibition of large number of oxidation states of actinides is due to the fact that there is a very small energy gap between 5f, 6d and 7s subshells and thus all their electrons can take part in bond formation.

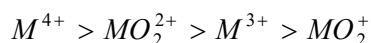


(ii) Actinide contraction: There is a regular decrease in ionic radii with increase in atomic number from Th to Lr. This is called actinide contraction analogous to the lanthanide contraction. It is caused due to imperfect shielding of one 5 f electron by another in the same shell. This results in increase in the effective nuclear charge which causes contraction in size of the electron cloud.

(iii) Color of the ions: Ions of actinides are generally colored which is due to f – f transitions. It depends upon the number of electrons in 5 f orbitals.

(iv) Magnetic properties: Like lanthanides, actinide elements are strongly paramagnetic. The magnetic moments are lesser than the theoretically predicted values. This is due to the fact that 5 f electrons of actinides are less effectively shielded which results in quenching of orbital contribution.

(v) Complex formation: Actinides have a greater tendency to form complexes because of higher nuclear charge and smaller size of their atoms. They form complexes even with  $\pi$ -bonding ligands such as alkyl phosphines, thioethers etc, besides EDTA,  $\beta$ -diketones, oxine etc. The degree of complex formation decreases in the order.



where M is element of actinide series. There is a high concentration of charge on the metal atom in  $MO_2^{2+}$  which imparts to it relatively high tendency towards complex formation.

