

Quadrant II – Transcript and Related Materials

Programme : Bachelor of Science (Second Year)

Subject : Chemistry

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Paper Title : Physical Chemistry and Inorganic Chemistry

Unit : I

Module Name : Lanthanides: Electronic Configuration, Oxidation States

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Notes

- Lanthanum (Z=57) and next fourteen elements (Z=58-71) which follow it are called **lanthanides**.
- The elements in which the additional electron enters (n-2) f-orbitals are termed as **inner transition elements**.
- These are also called as **F-block elements** because the extra electron enters f-orbitals which belong to (n-2)th shell.
- Lanthanum itself has been studied in d-block elements and not f-block.
- The f-orbital actually starts filling at cerium, Ce (Z=58), and is completely filled at lutetium, Lu (Z=71).
- Lanthanum is the element that proceeds lanthanide series,
- $\text{La} = 57 \ 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^{10} \ 4s^2 \ 4p^6 \ 4d^{10} \ 5s^2 \ 5p^6 \ 5d^1 \ 6s^2$ **OR** $[\text{Xe}]5d^1 \ 6s^2$
- Atomic number 58 the energy 4f-level falls below that 5d-level. And the electrons now enter inner 4f-orbitals.
- Lanthanum exhibits only the +3 oxidation state which is the most stable oxidation state of all the lanthanides (Ln^{3+}).
- Only +3 state is exhibited by La, Gd & Lu which is due to extra stability of empty, completely half filled or completely filled 4f-orbitals.
- $\text{La}^{3+} [\text{Xe}] 4f^0 \ 5d^0 \ 6s^0$; $\text{Gd}^{3+} [\text{Xe}] 4f^7 \ 5d^0 \ 6s^0$; $\text{Lu}^{3+} [\text{Xe}] 4f^{14} \ 5d^0 \ 6s^0$

- In addition to the usual +3 oxidation state, few of the lanthanides exhibit +2 and +4 oxidation states.
- The +2 and +4 oxidation states - Stable f^0 , f^7 and f^{14} configuration.
- For example: $Ce^{4+} = [Xe] 4f^0 5d^0 6s^0$ Empty
 $Tb^{4+} = [Xe] 4f^7 5d^0 6s^0$ Half Filled
 $Eu^{2+} = [Xe] 4f^7 5d^0 6s^0$ Half filled
 $Yb^{2+} = [Xe] 4f^{14} 5d^0 6s^0$ Completely filled
- It is not possible to explain certain oxidation states, e.g., Sm^{2+} having f^6 , Tm^{2+} having f^{13} , Pr^{4+} having f^1 , Nd^{4+} having f^2 configuration on the basis of extra stability.
- On the basis of highly complicated thermodynamic and kinetic consideration.
- The Ln^{4+} ions in aqueous solution have a tendency to change readily into M^{3+} ions. The standard potential of the half reaction involving reduction of Ce^{4+} , is $E^0 = 1.61$ volts.
- That indicates Ce^{4+} ion is strong oxidizing agent. Other $4+$ lanthanide ion like Pr^{4+} and Tb^{4+} are even more powerful oxidising agents.