Chemistry Study Materials for Class 12
(NCERT Based Revision Notes)
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d – Block Elements

GENERAL CHARACTERISTICS OF LANTHANIDES:

1. There are hard metals with high melting points.
2. **Oxidation state.** The lanthanides too display variable oxidation states. The characteristic and the most stable oxidation state of lanthanides is + 3 (Ln^{3+}). This oxidation state is obtained by the loss of one *5d*-electron and two *6s*-electrons. Along with + 3 oxidation state, certain metals show + 2 and + 4 oxidation states so as to attain f^{0}, f^{7} *and* f^{14} configurations.
3. **Ionic radii-Lanthanide contraction**. There is a regular decrease in the size of atoms/ions with increase in atomic number as we move across from La to Lu. Thus among lanthanides, lanthanum has the largest and lutetium has the smallest radii. This slow decrease in size is known as lanthanide contraction.

Cause of lanthanide contraction:

The configurations of lanthanides show that the additional electron enters the 4f- sub shell. The shielding of one *4f*-electron by another is very little (imperfect), being even smaller than that encountered in case of *d*-electrons (*d*-transition series). The imperfect shielding of f-electrons is due to the shape of *f*-orbitals which is very much diffused. Thus as the atomic number increases, the nuclear charge increases by unity of each stop, white no comparable increase in the mutual shielding effect of *4f*-electrons occurs. This causes a contraction in the size of the *4f*-subshell. Consequently the atomic and ionic size goes on decreasing systematically from *La* to *Lu*.

It must be noted that the decrease in atomic radii, although continuous, is not regular. The decrease is much more in the case of first six elements than in the subsequent elements. Hence the properties of lanthanide compounds show some divergence from regularity.

However, decrease in ionic radii is more regular.

Consequences of Lanthanide Contraction:

(i) Separation of Lanthanides: Separation of lanthanides is possible only due to lanthanide contraction. All the lanthanides have quite similar properties and due to this reason they are difficult to separate. However, because of lanthanide contraction their properties (such as ability to form complexes) vary slightly. This slight variation in properties is utilized in the separation of lanthanides by ion exchange methods.

(ii) Variation in basic strength of hydroxides: The basic strength of oxides and hydroxides decreases from La $(OH)_3$ to Lu $(OH)_3$. Due to lanthanide contraction size of M^{3+} ions decreases and there is increase in the cavalent character in M- OH bond.

(iii) Similarity of second and third transition series:The atomic radii of second row of transition elements are almost similar to those of the third row of transition elements. For example, among the elements of group 3, there is normal increase in size from Sc to Y to La. But after lanthanide the atomic radii from second to third transition series do not increase for group 4 and group 5. i.e., for Zr – Hf and Nb – Ta pairs which have element same atomic radii. After group 5 the effect of lanthanide contraction is not so predominant.

4. Colour: The lanthanide metals are silvery white but the trivalent lanthanide ions are coloured both in the solid state and in the aqueous solutions.

5. Magnetic properties: La^{3+} ($4f^0$) and Lu^{3+} ($4f^{14}$) having no unpaired electron do not show paramagnetism while all other tripositve ions of lanthanides are paramagnetic.

6. They have low ionization energy and are highly electropositive. Their ionization values are quite comparable with those of alkaline earth metals particularly calcium.

7. These metals do not have much tendency to form complexes.

8. The lanthanides are highly reactive. This is in agreement with the low value of their ionization energies.

9. The solubility of compounds of lanthanides follows the same order as group 2 elements. Their fluorides, oxides, hydroxides carbonates are insoluble in water. However halides (except fluorides), nitrates, acetates are soluble in water.

GENERAL CHARACTERISTICS OF ACTINIDES:

Actinides:

The elements with atomic numbers 90 to 103 i.e. thorium to lutetium (which come immediately after actinium, (Z = 89) are called actinides or actinoids. These elements involve the filling of *5f* 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 transuranic elements or transuranics which are produced artificially by nuclear reactions. They are synthetic or manmade. All actinides are radioactive.

Physico-chemical characteristics of Actinides:

(i) **Oxidation states:** These elements usually exhibit oxidation state of +2. However, they also show oxidation states of +4, +5 and +6.

(ii) **Physical state**: These are silvery white metals and get tarnished with alkalies.

(iii) **Density**: All the actinides except thorium and americium have high densities.

(iv) **Colour**: The actinide ions, in general are coloured. The colour depends upon the number of *5f*electrons. The ions of $5f^0$ *and* $5f^7$ configurations are colourless while ions with $5f^3$ *to* $5f^6$configfturations are coloured.

Li^{3+} ($5f^3$) :Red,

Np^{3+} ($5f^4$) : Bluish

Pu^{3+} ($5f^5$) :Blue

Am^{3+} ($5f^6$) : Pink

(v) **Ionisation energies**: These elements have low values of ionization energies.

(vi) **Electropositive character**: All the actinides are highly electropositive and as such are strong reducing agents.

(vii) **Complex formation**: Actinides have a strong tendency towards complex formation and form cations like , UO^{2+}, $PuO2^{2+}$, UO^{+} etc.

(viii) **Actinide contraction**: Actinides show actinide contraction. The size of atom/cation decreases regularly along the actinide series. The steady decrease in ionic radii with increase in atomic number is referred to as a actinide contraction. This is due to poor shielding of *5f* electrons.

Uses of Actinides:

(i) Plutonium as fuel for atomic reactors and in atomic bombs.

(ii) Uranium as nuclear fuel, its salts in glass industry (to impart colour), textile industry and in medicines.

(iii) Thorium in atomic reactors as fuel rods, in treatment of cancer, in gas mental (as a mixture of thorium and cerium nitrate 99:1)

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