

CHEMISTRY STUDY MATERIALS FOR CLASS 12

(NOTES BASED ON NCERT)

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The d & f - Block Elements

INNER TRANSITION ELEMENTS:

The elements which in their atomic or ionic form, in addition to their incomplete d -subshell of the penultimate shell have partly filled f -subshell of the ante-penultimate (inner to the penultimate shell i.e. $n-2$) shell are called as f -block elements. They are also known as inner transition elements. These are so called because these form a series within the transition series. The general electronic configuration of the f -block elements is $(n-2)f^{1-14} (n-1)s^2 (n-1) p^6 (n-1) d^{10} ns^2$.

Classification of f -block elements:

The f -block elements can be subdivided into two series depending upon the nature of the f -orbital of the antepenultimate shell ($4f$ or $5f$) in which the differentiating electron enters.

- (i) $4f$ -series (First inner transition series). In these the differentiating electron goes to $4f$ orbitals. This series consists of lanthanum ($Z = 57$) and the next 14 elements ($Z = 58$ to 71). These are known as Lanthanides.
- (ii) $5f$ -series (Second inner transition series). In these elements differentiating electron goes to $5f$ -orbitals. This series includes fifteen elements from actinium ($Z=89$) to Lawrencium ($Z = 103$). These are known as actinides. Inner transition elements are placed outside the body of the periodic table. The reason for this is the remarkable similarities among the chemical properties of lanthanides and also among the various members of the actinides. The similarities in properties, in turn is due to the similar electronic configuration of the outermost shell.

These elements differ only in the number of f electrons which do not take part in chemical bonding (difference from d-block elements in which the differentiating d-electrons are involved in chemical interaction).

LANTHANIDES OR LANTHANONS :

In these elements differentiating electron goes to *4f*-subshell. This series consists of 14 elements which follow lanthanum (Z = 57). It should be noted that fifteen elements starting from La57 to Lu71 are generally considered as lanthanides because they resemble one another closely. The name lanthanide has been derived from lanthanum which is the prototype of lanthanides. However, lanthanum is not an element of *f-block* of the periodic table.

Originally these elements were called rare earths because for many years pure compounds of these elements were difficult to obtain. Now a days the term rare earth is avoided because many of these elements are far from rare

Lanthanides				Actinides			
Name	Sym bol	At. No	Configuration	Name	Symb ol	At.N o.	Configuration
Cerium	Ce	58	[Xe]4f ² 5d ⁰ 6s ²	Thorium	Th	90	[Rn]5f ⁰ 6d ² 7s ²
Praseodymium	Pr	59	[Xe]4f ³ 5d ⁰ 6s ²	Protactinium	Pa	91	[Rn]5f ² 6d ¹ 7s ²
Neodymium	Nd	60	[Xe]4f ⁴ 5d ⁰ 6s ²	Uranium	U	92	[Rn]5f ³ 6d ¹ 7s ²
Promethium	Pm	61	[Xe]4f ⁵ 5d ⁰ 6s ²	Neptunium	Np	93	[Rn]5f ⁴ 6d ¹ 7s ²
Samarium	Sm	62	[Xe]4f ⁶ 5d ⁰ 6s ²	Plutonium	Pu	94	[Rn]5f ⁶ 6d ⁰ 7s ²
Europium	Eu	63	[Xe]4f ⁷ 5d ⁰ 6s ²	Americium	Am	95	[Rn]5f ⁷ 6d ⁰ 7s ²
Gadolinium	Gd	64	[Xe]4f ⁷ 5d ¹ 6s ²	Curium	Cm	96	[Rn]5f ⁷ 6d ¹ 7s ²
Terbium	Tb	65	[Xe]4f ⁹ 5d ⁰ 6s ²	Berkelium	Bk	97	[Rn]5f ⁸ 6d ¹ 7s ²
Dysprosium	Dy	66	[Xe]4f ¹⁰ 5d ⁰ 6s ²	Californium	Cf	98	[Rn]5f ¹⁰ 6d ⁰ 7s ²

Holmium	Ho	67	[Xe]4f ¹¹ 5d ⁰ 6s ²	Einsteinium	Es	99	[Rn]5f ¹¹ 6d ⁰ 7s ²
Erbium	Er	68	[Xe]4f ¹² 5d ⁰ 6s ²	Fermium	Fm	100	[Rn]5f ¹² 6d ⁰ 7s ²
Thulium	Tm	69	[Xe]4f ¹³ 5d ⁰ 6s ²	Mendelevium	Md	101	[Rn]5f ¹³ 6d ⁰ 7s ²
Ytterbium	Yb	70	[Xe]4f ¹⁴ 5d ⁰ 6s ²	Nobelium	No	102	[Rn]5f ¹⁴ 6d ⁰ 7s ²
Lutetium	Lu	71	[Xe]4f ¹⁴ 5d ¹ 6s ²	Lawrencium	Lr	103	[Rn]5f ¹⁴ 6d ¹ 7s ²

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 (Ln³⁺). 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- subshell. 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 step, while 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 $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$. Due to lanthanide contraction size of M^{3+} ions decreases and there is increase in the covalent 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:** $\text{La}^{3+} (4f^0)$ and $\text{Lu}^{3+} (4f^{14})$ having no unpaired electron do not show paramagnetism while all other tripositive 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 follow 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 actinones. 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, protoactinium and uranium and eleven transuranium elements or transuranics which are produced artificially by nuclear reactions. They are synthetic or man made. 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 alkalis.
- (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 $5f^6$ configurations 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+} , PuO_2^{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 an actinide contraction. This is due to poor shielding of $5f$ electrons.

Uses of Actinides:

- (i) Polonium 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 mantles (as a mixture of thorium and cerium nitrate 99:1)
