What are Lanthanides?

Lanthanides are the rare earth elements of the modern periodic table i.e. the elements with atomic numbers from **58 to 71 following element Lanthanum**. Since the occurrence (3×10^{-4} % of earth's crust) of these elements are very small they are called also like the **rare earth metals**. They are available in 'monazite' sand' as lanthanide orthophosphates. The lanthanide term first introduced by Victor Goldschmidt in 1925.

Element	Symbol	Atomic No.	Electronic configuration		Oxidation States		
			Atom	M^{3+}			
Lanthanum	La	57	2.8.18.18.8(1).2 [Xe]$4f^{0}5d^{1}6s^{2}$	[Xe]		**+3**	
Cerium	Ce	58	2.8.18.18(2).8.2 [Xe]$4f^{2}5d^{0}6s^{2}$	[Xe]$4f^{1}$		**+3**	+4
Praseodymium	Pr	59	2.8.18.18(3).8.2 [Xe]$4f^{3}5d^{0}6s^{2}$	[Xe]$4f^{2}$		**+3**	(+4)
Neodymium	Nd	60	2.8.18.18(4).8.2 [Xe]$4f^{4}5d^{0}6s^{2}$	[Xe]$4f^{3}$	(+2)	**+3**	
Promethium	Pm	61	2.8.18.18(5).8.2 [Xe]$4f^{5}5d^{0}6s^{2}$	[Xe]$4f^{4}$	(+2)	**+3**	
Samarium	Sm	62	2.8.18.18(6).8.2 [Xe]$4f^{6}5d^{0}6s^{2}$	[Xe]$4f^{5}$	(+2)	**+3**	
Europium	Eu	63	2.8.18.18(7).8.2 [Xe]$4f^{7}5d^{0}6s^{2}$	[Xe]$4f^{6}$	+2	**+3**	
Gadolinium	Gd	64	2.8.18.18(7).8(1).2 [Xe]$4f^{7}5d^{1}6s^{2}$	[Xe]$4f^{7}$		**+3**	
Terbium	Tb	65	2.8.18.18(9).8.2 [Xe]$4f^{9}5d^{0}6s^{2}$	[Xe]$4f^{8}$		**+3**	(+4)
Dysprosium	Dy	66	2.8.18.18(10).8.2 [Xe]$4f^{10}5d^{0}6s^{2}$	[Xe]$4f^{9}$		**+3**	(+4)
Holmium	Ho	67	2.8.18.18(11).8.2 [Xe]$4f^{11}5d^{0}6s^{2}$	[Xe]$4f^{10}$		**+3**	
Erbium	Er	68	2.8.18.18(12).8.2 [Xe]$4f^{12}5d^{0}6s^{2}$	[Xe]$4f^{11}$		**+3**	
Thulium	Tm	69	2.8.18.18(13).8.2 [Xe]$4f^{13}5d^{0}6s^{2}$	[Xe]$4f^{12}$	(+2)	**+3**	
Ytterbium	Yb	70	2.8.18.18(14).8.2 [Xe]$4f^{14}5d^{0}6s^{2}$	[Xe]$4f^{13}$	+2	**+3**	
Lutetium	Lu	71	2.8.18.18(14).8(1).2 [Xe]$4f^{14}5d^{1}6s^{2}$	[Xe]$4f^{14}$		**+3**	

Properties of Lanthanide Series

In the periodic table like transition metal if we consider lanthanides and actinides series the table will be too wide. These two series are present in the bottom of the periodic table and they are called 4f series (Lanthanods series) and 5f series (Actanoids series). The 4f and 5f series together called inner transition elements.

All of the elements in the series closely resemble lanthanum and each another in their chemical and physical properties. Some of the key characteristics and properties are:

- They have a lustre and are silvery in appearance.
- They are soft metals and can even be cut with a knife
- The elements have different reaction tendencies depending on basicity. Some are very reactive while some take time to react.
- Lanthanides can corrode or become brittle if they are contaminated with other metals or non-metals.
- They all mostly form a trivalent compound. Sometimes they can also form divalent or tetravalent compounds.
- They are magnetic.

Lanthanide Contraction

The atomic size or the ionic radii of tri positive lanthanide ions decrease steadily from La to Lu due to increasing nuclear charge and electrons entering inner (n-2) f orbital. This gradual decrease in the size with an increasing atomic number is called **lanthanide contraction.**

⇒ **Also Read:** Actinides

Consequences of Lanthanide Contraction

Following points will clearly depict the effect of lanthanide contraction:

- Atomic size
- Difficulty in the separation of lanthanides
- Effect on the basic strength of hydroxides
- Complex formation
- The ionization energy of d-block elements

1. **Atomic size:** Size of the atom of third transition series is nearly the same as that of the atom of the second transition series. For example: radius of Zr = radius of Hf & radius of Nb = radius of Ta etc.

2. **Difficulty in the separation of lanthanides**: As there is an only small change in the ionic radii of Lanthanides, their chemical properties are similar. This makes the separation of elements in the pure state difficult.

3. Effect on the basic strength of hydroxides: As the size of lanthanides decreases from La to Lu, the covalent character of the hydroxides increases and hence their basic strength decreases. Thus, La (OH)3 is more basic and Lu(OH)3 is the least basic.

4. Complex formation: Because of the smaller size but higher nuclear charge, tendency to form coordinate. Complexes increases from La3+ to Lu3+.

5. Electronegativity: It increases from La to Lu.

Electronic Configuration of Lanthanides

Lanthanides of first f-block have a terminal electronic configuration of [Xe] 4f1-14 5d 0-16s2 of the fourteen lanthanides, promethium (Pm) with atomic number 61 is the only synthetic radioactive element. The energy of 4f and 5d electrons are almost close to each other and so 5d orbital remains vacant and the electrons enter into the 4f orbital.

Exceptions are in the case of gadolinium, Gd (Z = 64) where the electron enters the 5d orbital due to the presence of half-filled d-orbital and lutetium (Z = 71) enters the 5d orbital.

Oxidation State of Lanthanides

All the elements in the lanthanide series show an oxidation state of +3. Earlier it was believed that some of the metals (samarium, europium, and ytterbium) also show +2 oxidation states. Further studies on these metals and their compounds have revealed that all the metals in lanthanide series exhibit +2 oxidation state in their complexes in solutions.

A few metals in the lanthanide series occasionally show +4 oxidation states. This uneven distribution of oxidation state among the metals is attributed to the high stability of empty, half-filled or fully filled f-subshells.

The stability of f-subshell affects the oxidation state of lanthanides in such a way that the +4 oxidation state of cerium is favoured as it acquires a noble gas configuration but it reverts to a +3 oxidation state and thus acts as a strong oxidant and can even oxidize water, although the reaction will be slow.

The +4 oxidation state is also exhibited by the oxides of:

- Praseodymium (Pr)
- Neodymium (Nd)
- Terbium (Tb)
- Dysprosium (Dy)

Europium (atomic number 63) has the electronic configuration [Xe] $4f^7$ $6s^2$, it loses two electrons from 6s energy level and attains the highly stable, half-filled $4f^7$ configuration and hence it readily forms Eu^{2+}ion. Eu^{2+} then changes to the common oxidation states of lanthanides (+3) and forms Eu^{3+}, acting as a strong reducing agent.

Ytterbium (atomic number 70) also has similar reasons for being a strong reducing agent, in the Yb^{2+} state; it has a fully filled f-orbital.

The presence of f-subshell has a great influence on the oxidation state exhibited by these metals and their properties. New developments and findings continue to add information on lanthanides.

The energy gap between 4f and 5d orbitals is large and so the number of oxidation states limited, unlike the d-block elements.

Why Lanthanide show Variable Oxidation State?

Lanthanides show variable oxidation states. They also show **+2, +3, and +4 oxidation states**. But the most stable oxidation state of Lanthanides is +3. Elements in other states hence try to lose or gain electrons to get +3 state. By that those ions become strong reducing or oxidizing agents respectively.

Oxidation state in Aqueous Solution

In aqueous solution, Sm^{2+}, Eu^{2+} and Yb^{2+} loose electron, ie get oxidized and are good reducing agents. On the other hand Ce^{4+}, Pr^{4+}, Tb^{4+} gain electron – gets reduced and are good oxidizing agents. Higher oxidation states (+4) of elements are possible only with oxides. **Example:** Pr, Nd, Tb and Dy.

3. Magnetic Properties: Materials are classified by their interaction with the magnetic field as:

- Diamagnetic if repelled
- Paramagnetic if attracted

The lanthanide atoms/ions other than f0 and f14 type are paramagnetic in nature due to unpaired electrons in orbitals. Hence Lu^{3+}, Yb^{2+} and Ce^{4+} are diamagnetic.

Unpaired electrons contribute to 'orbital magnetic moment' and 'spin magnetic moment'. Orbital angular moment and spin magnetic moment of the electrons are taken into account for calculating the total magnetic moment.

$M = \sqrt{[4S(S+1)+L(L+1)]}$ BM and its unit is Bohr Magneton (BM)

Formation of Coloured Ions

Lanthanides ions can have electrons in f-orbital and also empty orbitals like the d-block elements. When a frequency of light is absorbed, the light transmitted exhibit a colour complementary to the frequency absorbed. Inner transition element ions can absorb the frequency in the visible region to use it for f-f electron transition and produce visible colour.

Many of the lanthanide metals are silver-white. The lanthanide ions with +3 oxidation state are coloured both in solid-state and in aqueous solution.

The colour of a cation depends on the number of unpaired f electrons Lanthanides, with xf electrons, have the same colour as of (14-x) electron elements.