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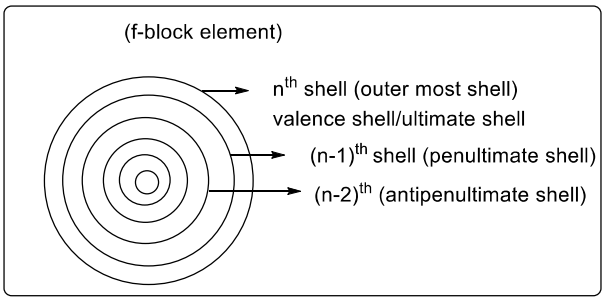
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# CHAPTER - 1

# INNER TRANSITION ELEMENTS

## 1.1. Introduction




In this chapter we look at f-block metals and their compounds. There are two series of metals: *the lanthanoids* (the 14 elements that follow lanthanum in the periodic table) and *the actinoids*(the 14 elements following actinium).

- **The lanthanoids are electropositive metals that commonly occur in their compounds as Ln (III); other oxidation states are stable only when an empty, half-filled, or full f subshell is produced.**
- **Lanthanides are characterized by the filling up of the antepenultimate 4*f* energy levels.**
- **Actinides are characterized by the filling up of the antepenultimate 5*f* energy levels.**

They are extremely similar to each other in properties, and until 1907 they were thought to be a single element. In the past they were called the rare earths. This name is not appropriate because many of the elements are not particularly rare. Furthermore, the name is not precise since in addition to the 14 lanthanides it also includes La, Sc, Y which are d-block elements, and sometimes Th (an actinide) and Zr (another d-block element).

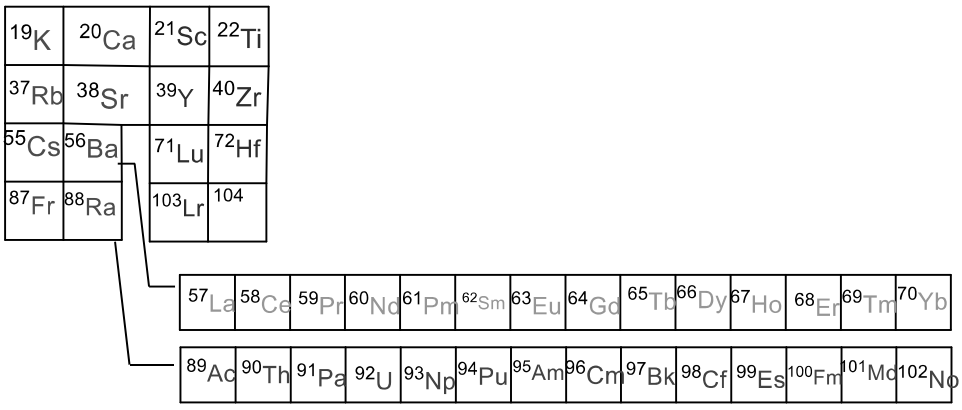



**Fig 1.1: Position in the periodic table**

## 1.2. Electronic Structure of Lanthanides

The electronic structures of the lanthanide metals are shown in Table-1. Lanthanum (the d-block element preceding this series) has the electronic structure: xenon core $4f^0 5d^1 6s^2$. It might be expected that the 14 elements from cerium to lutetium would be formed by adding 1, 2, 3, ... 14 electrons into the 4*f*level.However, it is energetically favourable to move the single 5*d* electron into the 4*f* level in most of the elements, but not in the cases of Ce, Gd and Lu.The reason why Gd has a $5d^1$arrangement is that this leaves a half filled 4*f* level, which gives increased stability i.e. $[Xe]4f^7\ 5d^1\ 6s^2$.Lu has a $5d^1$ arrangement because the *f* shell is already full. i.e.**[Xe] 4f14 $5d^1$ $6s^2$**

The lanthanides are characterized by the uniform (+III) oxidation state shown by all the metals. They typically form compounds which are ionic and trivalent. The electronic structures of the ions are $Ce^{3+}$-$f^1$, $Pr^{3+}$-$f^2$, $Nd^{3+}$-$f^3$..... $Lu^{3+}$-$f^{14}$.

Electrons are filled in the 4f subshell which is antepenultimate shell (inside penultimate shell i.e.d subshell) 4f electrons are very effectively shielded from their chemical environment outside the atom by the 5s and 5*p* electrons. Consequently, the 4*f* electrons do not take part in bonding. They are neither removed to produce ions nor do they take any significant part in crystal field stabilization of complexes. So the oxidation state shown by these metals is due to loss of electrons from outer d and s orbitals.

Crystal field stabilization is very important with the d-block elements. The octahedral splitting of *f*orbitals,$\Delta_0$ is only about I kJ mo1-1. So, whether the *f* orbitals are filled or empty has little effect on the normal chemical properties. However, it does affect their spectra and their magnetic properties.

**Table 1.1: Electronic Structures and Oxidation States**

| Element and their symbols | | Electronic Structure of Atoms | Electronic Structure of $M^{3+}$ | Oxidation States |
|---|---|---|---|---|
| Lanthanum | La | $[Xe]\ 5d^1\ 6s^2$ | [Xe] | +III |
| Cerium | Ce | $[Xe]4f^1\ 5d^1\ 6s^2$ | $[Xe]4f^1$ | +III +IV |
| Prascodymium | Pr | $[Xe]4f^3 6s^2$ | $[Xe]4f^2$ | +III (+IV) |
| Neodymium | Nd | $[Xe]4f^4\ 6s^2$ | $[Xe]4f^3$ | (+II) +III |
| Promethium | Pm | $[Xe]4f^5 6s^2$ | $[Xe]4f^4$ | (+II) +III |
| Samarium | Sm | $[Xe]4f^6\ 6s^2$ | $[Xe]4f^5$ | (+II) +III |
| Europium | Eu | $[Xe]4f^7\ 6s^2$ | $[Xe]4f^6$ | +II +III |
| Gadolinium | Gd | $[Xe]4f^7 5d^1\ 6s^2$ | $[Xe]4f^7$ | +III |
| Terbium | Tb | $[Xe]4f^9\ 6s^2$ | $[Xe]4f^8$ | +III (+IV) |
| Dysprosium | Dy | $[Xe]4f^{10}6s^2$ | $[Xe]4f^9$ | +III (+IV) |
| Holmium | Ho | $[Xe]4f^{11}6s^2$ | $[Xe]4f^{10}$ | +III |
| Erbium | Er | $[Xe]4f^{12}6s^2$ | $[Xe]4f^{11}$ | +III |
| Thulium | Tm | $[Xe]4f^{13}\ 6s^2$ | $[Xe]4f^{12}$ | (+II) +III |
| Ytterbium | Yb | $[Xe]4f^{14}\ 6s^2$ | $[Xe]4f^{13}$ | +II +III |
| Lutetium | Lu | $[Xe]4f^{14}\ 5d^1\ 6s^2$ | $[Xe]4f^{14}$ | +III |

**Q1. Which of the following carbonate- fluoride mineral contains all the lanthanoids?**

a. Monazite b.Bastnasite

c. Pitch blende d.Zicronite

**Solution:**

Bastnasite mainly represented by (Ce, La, Y) $CO_3F$ contains all the lanthanoids, whereas Monazite (Phosphate mineral of thorium and other rare earth) contains lines ones.

## 1.3. Physical Properties:

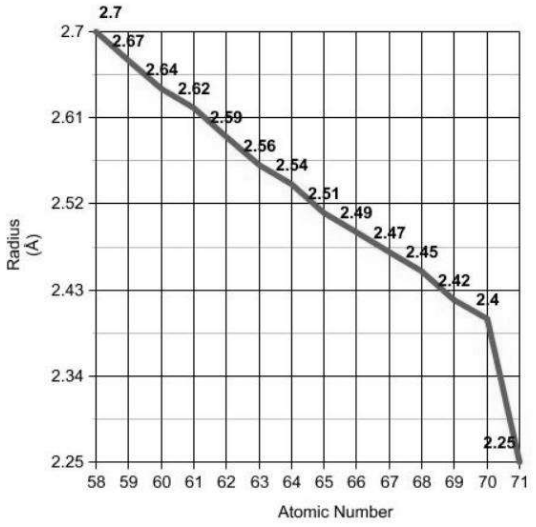
### 1.3.1. Ionic Radius

Ionic radii depend on how many electrons are removed. For simplicity, the radii of ions with the same charge are compared in Table.

**Table 1.2: Ionic Radii of $Sc^{3+}$, $Y^{3+}$ and $La^{3+}$ and the $Ln^{3+}$ ions ($A^0$)**

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sc | | | | | | | | | | | | |
| 0.745 | | | | | | | | | | | | |
| Y | | | | | | | | | | | | |
| 0.900 | | | | | | | | | | | | |
| La | Ce | Pr | Nd | Pm | SmEuGd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| 1.03 | 1.02 | 0.99 | 0.983 | 0.97 | 0.958 | 0.947 | 0.938 | 0.923 | 0.912 | 0.901 | 0.890 | 0.88 |
| 0.868 | 0.861 | | | | | | | | | | | |

A similar change in size across the series is observed if covalent radii are compared (Table 3). Because of this contraction in size across the lanthanide series, the elements which follow in the third transition series are considerably smaller than would otherwise be expected. The normal size increase Sc→ Y→ La uisappears after the lanthanides. Thus, pairs of elements such as Zr/Hf, Nb/Ta and Mo/W are almost identical in size. The close similarity of properties in such a pair makes chemical separation very difficult. The sizes of the third row of transition elements are very similar to those of the second row of transition elements (see Table). *Thus, the second and third rows of transition elements resemble each other more closely than do the first and second rows.*



### 1.3.2. Oxidation states

The sum of the first three ionization energies for each element is given in Table-4. The values are low. Thus, the oxidation state (+III) is ionic and $Ln^{3+}$ dominates the chemistry of these elements. The $Ln^{2+}$ and $Ln^{4+}$ ions that do occur are always less stable than $Ln^{3+}$. *(In this chapter the symbol Ln is used to denote any of the lanthanides).*

In just the same way as for other elements, the higher oxidation states occur in the fluorite and oxides, and the lower oxidation states occur in the other halides particularly bromides and iodides.

Oxidation numbers (+II) and (+IV) do occur particularly when they lead to:

a. A noble gas configuration. e.g. $Ce^{4+}$ ($f^0$)
b. A half-filled*f*shell. E.g. $Eu^{2+}$ and $Tb^{4+}$ ($f^7$)
c. A completely filled *f level*. e.g. $Yb^{2+}$ ($f^{14}$)

In addition (+II) and (+IV) states exist for elements that are close to these states. Thus $Sm^{2+}$ and $Tm^{2+}$ occur with $f^6$ and $f^{13}$ arrangements and $Pr^{2+}$ and $Nd^{4+}$ have $f^1$ and $f^2$ arrangements. The (+III) state is always the most common and the most stable.Theonly (+IV) and (+II) states which have any aqueous chemistry are $Ce^{4+}$, $Sm^{2+}$, $Eu^{2+}$ and $Yb^{2+}$.The lanthanide elements resemble each other much more closely than a horizontal row of the transition elements.This is because the lanthanides effectively have only one stable oxidation state, (+III).

**The stability of the elements in the different oxidation states givevs the information about the oxidizing power and reducing power of that particular element. This can be illustrated by the followmg three examples:**

a. **$Ce^{4+}$ is a strong oxidising reagent**:
   Electronic configuration of Ce is $4f^15d^16s^2$. Ce is most stable in +3 state. In +4 state it is most oxidizing because in +4 state it can give an electron to become more stable at +3 state.
   **CAN (Ceric Ammonium Nitrate) is a stronger reagent than $KMNO_4$ and $K_2Cr_2O_7$ in some reactions.**

b. **$Eu^{2+}$ is a strong reducing reagent**:
   $Eu^{2+}$ is less stable than that of the $Eu^{3+}$ due to configurational reasons as stated in the above table. Thus $Eu^{2+}$ acts as a strong reducing agent.

c. **$Sm^{2+}$ is a strong oxidising reagent**:
   Whereas in $Sm^{+2}$, the lanthanides are more stable in +3 state and hence in +2 state it gets oxidized easily (good reducing agent) to get to +3 oxidation state.

### 1.3.3. Ionization Energy

Lanthanides have fairly low ionisation energies. $IE_1$and $IE_2$values are quite comparable with the values of alkaline earthmetals, particularly calcium. The sum of the first three ionisation energies in kJ/mol for each element is given below. Thevalues are low.

Due to low values of ionisation energies, lanthanides are highly electropositive in nature. The values of standard reduction potential (E values) increase from La to Lu. $E^0$values become less negative in the series. Although there are some exceptions, All the lanthanides are, thus, strong **reducing agents.** The reducing power decreases from La to Lu.

The values in volts are given in the following table:

**Table 1.3: Ionization Energy and Standard Electrode Potential**

| Elements | Symbol | Sum of first three ionisation energies (kJ $mol^{-1}$) | Eo $Ln^{3+}$/ Ln(volts) | Radius $Ln^{3+}$ (Å) |
|---|---|---|---|---|
| **Lanthanum** | **La** | **3493** | **-2.52** | **1.032** |
| **Cerium** | Ce | 3512 | -2.48 | 1.020 |
| **Praseodymium** | Pr | 3623 | -2.46 | 0.99 |
| **Neodymium** | Nd | 3705 | -2.43 | 0.983 |
| **Promethium** | Pm | - | -2.42 | 0.97 |
| **Samarium** | Sm | 3898 | -2.41 | 0.958 |
| **Europium** | Eu | 4033 | -2.41 | 0.947 |
| **Gadolinium** | Gd | 3744 | -2.40 | 0.938 |
| **Terbium** | Tb | 3792 | -2.39 | 0.923 |
| **Dysprosium** | Dy | 3898 | -2.35 | 0.912 |
| **Holmium** | Ho | 3937 | -2.32 | 0.901 |
| **Erbium** | Er | 3908 | -2.30 | 0.890 |
| **Thulium** | Tm | 4038 | -2.28 | 0.880 |
| **Ytterbium** | Yb | 4197 | -2.27 | 0.868 |
| **Lutetium** | Lu | 3898 | -2.26 | 0.861 |

**The point to be noted that is, the first ionization energies of Sm, Dy and Lu are same.**

**Q. Which statement is incorrect about the lanthanoid metals?**

**a**. Each metal reacts with dilute acid to release $H_2$.

**b**.Eu and Yb dissolve in liquid $NH_3$ to give $Eu^{3+}$ and $Yb^{3+}$ respectively.

**c**. Reaction between Ln and $H_2$ give hydrides of formula $LnH_2$ or $LnH_3$.

**d**. The chemistry of the lanthanoids is dominated by the +3-oxidation state

**Solution: 2**

$Eu^{3+}$ and $Yb^{3+}$ are formed

$Eu^{2+}$ has $4f^7$ configuration. -very stable

$Yb^{2+}$ has $4f^{14}$ configuration – appreciably stable

### 1.3.4. Shielding effect of the lanthanoids

The Lanthanide Contraction is the result of a poor shielding effect of the 4f electrons. The shielding effect is described as the phenomenon by which the inner-shell electrons shield the outer-shell electrons so they are not

affected by nuclear charge. So when the shielding is not as good, this would mean that the positively charged nucleus has a greater attraction to the electrons, thus decreasing the atomic radius as the atomic number increases. The s orbital has the greatest shielding while f has the least and p and d in between the two with p being greater than d. The Lanthanide Contraction can be seen by comparing the elements with f electrons and those without f electrons in the d block orbital. Pd and Pt are such elements. Pd has 4d electrons while Pt has 5d and 4f electrons. These 2 elements have roughly the same atomic radius. This is due to Lanthanide Contraction and shielding. While we would expect Pt to have a significantly larger radius because more electrons and protons are added, it does not because the 4f electrons are poor at shielding. When the shielding is not good there will be a greater nuclear charge, thus pulling the electrons in closer, resulting in a smaller than expected radius.

**1.3.5. Hydration energy and lattice energy: -**

- **Hydration energy** (also hydration enthalpy) is the amount of energy released when one mole of ions undergo hydration which is a special case of solvation. It is a special case of dissolution energy, with the solvent being water.
- **Lattice energy is** a measure of the energy contained in the crystal lattice of a compound, equal to the energy that would be released if the component ions were brought together from infinity.
- **It is found that- "**Small elements have high lattice and hydration energy. As the size increases, lattice energy and hydration energy are found to be decreased.**"**

**Thus from La to Lu, Lattice energy and hydration energy decreases as expected.**

**1.3.6. Abundance and Isotopes**

The lanthanide elements are not particularly rare. Cerium is about as abundant as copper. Apart from promethium, which does not occur in nature, all the elements are more abundant than iodine. The abundance of the elements and the number of naturally occurring isotopes varies regularly (**Table 5**). Elements with an even atomic number (i.e. an even number of protons in the nucleus) are more abundant than their neighbours with odd atomic numbers *(Harkins' rule).*

Elements with even atomic numbers also have more stable isotopes. Elements with odd atomic numbers never have more than two stable isotopes. Throughout the periodic table the stability of a nucleus is related to both the number of neutrons and the number of protons in the nucleus (**Table 6**). **Element 61, promethium, does not occur naturally**. It was first made and studied at Oak Ridge in Tennessee, USA, in 1946. Its absence may be explained by Mattauch's rule.

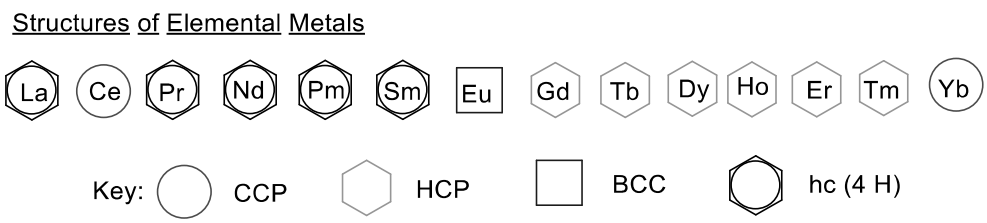
This states that if two elements with consecutive atomic numbers each have an isotope of the same weight, one of the isotopes will be unstable. Since elements 60 and 62 have seven isotopes each, there are not many stable mass numbers available for promethium, element 61 (**Table 6**). According to Matrauch's rules, if promethium is to have a stable isotope, it must have a mass number outside the range 142-150. The only isotopes of Pm which have been made so far are radioactive.

**Table 1.4: Abundance of the elements in the earth's crust by weight and number of natural isotopes**

| Atomic number | Element | Abundance (ppm) in earth's crust | Relative abundance | Naturally occurring isotopes |
|---|---|---|---|---|
| 58 | Ce | 66 | 26 | 4 |
| 59 | Pr | 9.1 | 37 | 1 |
| 60 | Nd | 40 | 27 | 7 |
| 61 | Pm | 0 | 32 | 0 |
| 62 | Sm | 7 | 40 | 7 |
| 63 | Eu | 2.1 | 49 | 2 |
| 64 | Gd | 6.1 | 41 | 7 |
| 65 | Tb | 1.2 | 56 | 1 |
| 66 | Dy | 4.5 | 42 | 7 |
| 67 | Ho | 1.3 | 55 | 1 |
| 68 | Er | 3.5 | 43 | 6 |
| 69 | Tm | 0.5 | 61 | 1 |
| 70 | Yb | 3.1 | 44 | 7 |
| 71 | Lu | 0.8 | 59 | 2 |

**Table 1.5. Numbers of stable nuclei with odd and even numbers of neutrons and odd and even atomic number**

| Atomic number | Number of neutrons | Stable nuclei |
|---|---|---|
| Even | Even | 164 |
| Even | Odd | 55 |
| Odd | Even | 50 |
| Odd | Odd | 4 |




**Q1. What is the difference between lanthanoids and lanthanides?**

**Solution:** Fifteen elements from La-Lu are **lanthanoids.** (Preferred by IUPAC).Furthermore, fourteen elementCe-Lu without lanthanum are **lanthanides** (meaning the elements similar to lanthanum).