ATOMIC ENERGY CENTRAL SCHOOL-3

MODULE-2

UNIT : d and f- BLOCLK ELEMENTS

CHAPTER : f- BLOCK ELEMENTS

SYLLABUS

- Lanthanoids – electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction and its consequences. Actinoids – Electronic configuration, oxidation states and comparison with lanthenoids .

INTRODUCTION

f-block elements :

Elements of 6^{th} & 7^{th} periods in which last electron enters in (n-2) f –subshell of their atoms are called as f-block elements. They are also called as inner transition elements because they form a transition series whithin the the transition elments(d-block elements). Their percentage abundance in earth crust is very less therefore they are also called as rare earth elements.

Classification of f-block elements

- Depending upon whether the last electron (also called differentiating electron) enters in a 4f-orbital or 5f-orbital,

the f-block elements have been divided into two series as follows:

(a) Lanthanoids(or Lanthanons) : These are the 14 –elements from $_{53}$La to $_{71}$ Lu, these elements called lanthanoids due to following reasons:

(i) they are following La, means their properties and properties of La are quite similar.

(ii) they come immediately after La.

series of 14 elements here is called as lanthanoid series. They are also called 4f-block elements and series here is called as 4f series because in these 14 elements last electron enters in one of the 4f orbital.

These are Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

Classification of f-block elements

(b) Actinoids(or actinons) : These are the 14 –elements from

$_{89}$Ac to $_{103}$Lr, these elements called actinoids due to following reasons:

(i) they are following Ac, means their properties and properties of Ac are quite similar.

(ii)they come immediately after Ac.

series of 14 elements here is called as actinoid series. They are also called 5f-block elements and series here is called as 5f series because in these 14 elements last electron enters in one of the 5f orbital.

These are Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr.

Electronic configuration

Their(f-block elements or inner transition elements or lanthanides & actinides) general electronic configuration:

$(n-2)\ f^{1-14}\ (n-1)\ d^{0-1}\ ns^{2}$.

General electronic configuration of Lanthanides is $[Xe]4f^{1-14}\ 5d^{0-1}\ 6s^{2}$

General electronic configuration of actinides is $[Rn]5f^{1-14}\ 6d^{0-1}\ 7s^{2}$

Oxidation states (Lanthanides)

- The typical oxidation state of the Lanthanides is +3. The oxidation state +2 and +4 also shown by some of the elements which can acquire stable configuration of f^0, f^7 or f^{14} , e.g. Eu^{2+} or Tb^{2+} =[Xe]$4f^7$, Yb^{2+}= [Xe]$4f^{14}$, Ce^{4+}=[Xe] $4f^0$.
- Each case tends to revert to the more stable +3 state by loss of gain of electron. This is why Eu^{2+} and Yb^{2+} ions in solution are good reducing agent while Ce^{4+} is a good oxidising agent.

Chemical reactivity (Lanthanides)

- The first few members of the series are quite reactive almost like calcium. However, with increasing atomic number, their behavior become similar to that of aluminum.
- They combine with $H_2(g)$ on gentle heating :

  $2Ln + 3H_2 \longrightarrow 2\,LnH_3$.
- When heated with C, forms carbides of formula Ln_3C , Ln_2C_3, LnC_2 .

  $2Ln + 4\,C \longrightarrow 2\,LnC_2$.
- On burning in the presence of halogens, they form halides:

  $2Ln + 3\,X_2 \longrightarrow 2LnX_3$
- They react with dilute acids to liberate $H_2(g)$:

  $2Ln + 6HCl \longrightarrow 2LnCl_3 + 3\,H_2(g)$
- They form oxide on burning in oxygen :

  $4Ln + 3\,O_2 \longrightarrow 2Ln_2\,O_3$
- They form hydroxide on reaction with water .

Hydroxides and oxides of lanthanides are basic like alkaline earth metal oxides and hydroxides.

Here Ln is stand for Lanthanide metal.

Lanthanoid contraction

- In lanthanides series, with increase in atomic number, there is a progressive decrease in the atomic and ionic radii of the lanthanides, this regular decrease in the atomic and ionic radii with increasing atomic number is called as Lanthanoid contraction.

- **Cause of lanthanoid contraction** : As we move along the lanthanide series, the nuclear charge increasing by one unit at each successive member. The new electron is added into the one of the orbital of 4f subshell, the shielding of 4f- electrons is poor can not counterbalance the effect of the increased nuclear charge. Hence, the net result is a regular contraction in the size of atom or ion, on moving to lower member to higher member in this series.

Consequences of Lanthanide contraction

- **Difficulty in separation of lanthanides** : Since the change in ionic radii in the lanthanides is very small and we know that chemical properties depend on the size of atom or ion so the chemical properties of these elements are similar this makes the separation of the lanthanides difficult. But lanthanoid contraction results in slight difference in size of the atom or ion of lanthanoids which result in the differences in properties due to that it is possible to separate individual lanthanoid by ion exchange method.
- **Difficulty in separation of 2d & 3d elements** The almost identical radii of Zr(160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.
- **Effect on basic strength of hydroxides** : As the size of the lanthanide ions decreases due to lanthanide contraction from La^{3+} to Lu^{3+}, the covalent character of the hydroxides increases hence the basic strength decreases. Thus, $La(OH)_3$ is more basic than $Lu(OH)_3$.

Actinides

- General electronic configuration of actinides is $[Rn]5f^{1-14}\ 6d^{0-1}\ 7s^{2}$

Actinides or Actinons or Actinoids

- **Oxidation states** : There is a greater range of oxidation states, which is in part attributed to the fact that the *5f, 6d and 7s levels are of comparable energies.* The actinoids show in general +3 oxidation state. The elements, in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements i.e Am -Lr .The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse. Because the distribution of oxidation states among the actinoids is so

uneven and so different for the former and later elements, it is unsatisfactory to review their chemistry in terms of oxidation states.

Comparison of actinides and lanthanides

Similarities :

- The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state.
- Both are metallic and very reactive.
- Both exhibit magnetic and spectral properties.
- Actinides exhibit actinide contraction like lanthanide contraction.

- **Differences :**

Actinides are radioactive, have greater tendency towards complex formation.

Beside +3 oxidation state, they show higher oxidation states of +4, +5, +6, +7 .

Actinides form oxocations e.g. UO_2^{2+} , PuO_2^{2+} .

Most of the ions of Actinides are coloured .

The- End