"बेटी बचाओ, बेटी पढ़ाओ"

JAYOTI VIDYAPEETH WOMEN'S UNIVERSITY, JAIPUR

Faculty of Education & Methodology

Faculty Name	-	JV'n Dr. Mangat Singh (Assistant Professor)
Program	-	V/2023-Semester / Year
Course Name	–	(B.Sc. B.Ed. ZBC/PCM)-V-SEM

Academic Day starts with –

- Greeting with saying **'Namaste'** by joining Hands together following by 2-3 Minutes Happy session, Celebrating birthday of any student of the respective class and **National Anthem**.

Lecture Starts with-

- Topic to be discussed today- **F-BLOCK ELEMENTS**
- Introduction & Brief Discussion aboutthe Topic

  The elements in which the last electrons enter into anti-penultimate shell-(n – 2)f orbitals are called f-block elements or inner transition elements. The general electronic configuration of such elements can be represented as $(n-2)\ f^{0-14}(n-1)d^{0,1,2}\ ns^2$. The elements of 4f-block elements are also known as Lanthanides or rare earth elements. Similarly, 5f-block elements are typically called actinides. The names Lanthanides and Actinide have been given due to their close resemblance with Lanthanum and Actinium respectively.University Library Reference- *Concise Inorganic Chemistry by J D Lee*

- Questions to check the understanding level of students-
    1. Why +3 oxidation state is stable in *f-block elements*
    2. Explain the exceptional electronic configuration in ***f-block elements***
- Small Discussion About Next Topic- ***Separation of f-block elements***

f-block elements:

INTRODUCTION

Inner transition elements/f-block elements

The elements in which the last electrons enter into anti-penultimate shell-(n – 2)f orbitals are called f-block elements or inner transition elements. The general electronic configuration of such elements can be represented as $(n\text{-}2)\ f^{0\text{-}14}(n-1)d^{0,1,2}\ ns^2$. The elements of 4f-block elements are also known as Lanthanides or rare earth elements. Similarly, 5f-block elements are typically called actinides. The names Lanthanides and Actinide have been given due to their close resemblance with Lanthanum and Actinium respectively. Lanthanides constitute the first inner transition series while actinides constitute second inner transition series.

General Characteristics:

Electronic Configuration: $[Xe]\ 4f^{0\text{-}14}\ 5d^1 6s^2$

Oxidation state: F-block readily forms M+3 ions and therefore the common oxidation state is +3. However, some of the elements exhibit oxidation states of +2 and +4 as they acquire stable electronic configuration in this oxidation state

Colouration: F-block elements exhibit colour not only in the solid state but also in an aqueous solution because, after the absorption of light, they undergo f-f-transition since they have partly filled f-orbitals.

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

Illustration: What is the basic difference between the electronic configuration of transition and inner transition elements?

Sol: General electronic configuration of transition elements = [Noble gas] $(n – 1) d^{1–10} ns^{1–2}$ and for inner transition elements = $(n – 2) f^{1–14}(n – 1)d^{0–1} ns^{0–2}$. Thus, in transition elements, the last electron enters the d-orbitals of the penultimate shell while in inner transition elements, it enters the f-orbital of the penultimate shell.

Illustration: What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements: 29, 59, 74, 95, 102, 104.

Sol: Inner transition elements are those that have incomplete 4f of 5f orbitals. Thus 59, 95 and 102 are inner transition elements.

LANTHANIDES AND THEIR PROPERTIES

The lanthanide series of chemical elements comprises fifteen metallic chemical elements with atomic numbers 57 through 71, from lanthanum through lutetium. These fifteen lanthanide elements, along with the chemically similar elements, scandium and yttrium, are often collectively known as the rare earth elements.

Lanthanide Contraction

In lanthanides, the additional electron enters the 4f-sub shell but not in the valence shell i.e. sixth shell. The shielding effect of one electron in 4f-sub-shell by another in the same sub-shell is very little, being even smaller than that of d-electrons, because the shape of f-sub shell is very much diffused, while there is no comparable increase in the mutual shielding effect of 4f-electrons. This results in outermost shell electrons in the experience increasing nuclear attraction from the growing nucleus. Consequently, the atomic and ionic radii go on decreasing as we move from La^{57} to Lu^{71}.

Consequence of Lanthanide contraction

Atomic and ionic radii of post-Lanthanide elements: The atomic radii of second-row transition elements are almost similar to those of the third-row transition elements because the increase in size on moving down the group from second to third transition elements is cancelled by the decrease in size due to lanthanide contraction.

High density of Lanthanide elements: It is because of a very small size due to lanthanide contraction and increase in molar mass.

Basic strength of oxides and hydroxides: Due to lanthanide contraction, the decrease in size of lanthanides ions, from La^{3+} to $Lu3^{+}$ increases the covalent character (i.e. decreases the ionic character) between Ln^{+3} and OH– ions in Ln(III) hydroxides (Fajan’s rules). Thus $La(OH)_3$ is the most basic while Lu(OH)3 is the least basic. Similarly, there is a decrease in the basic strength of the oxides.

Separation of Lanthanides: Due to the similar size (lanthanide contraction) of the lanthanides, it is difficult to separate them. But a slight variation in their properties is utilized to separate.

Illustration: Why is the separation of lanthanoids difficult? Explain.

Sol: All the Lanthanoid ions are of almost the same size, so they have almost similar chemical and physical properties and thus their separation becomes difficult.

Illustration: Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behavior with the electronic configuration of these elements.

Sol: +4 = Ce, Pr, Nd, Tb, Dy. +2 = Eu, Yb. These states are accounted by the extra stability of half-filled and completely filled f-orbitals.

Chemical Reactivity

These are very reactive metals like alkaline earth metals; however, they show very little difference in their chemical reactivity. On strong heating with H_2 and carbon, these form salt like non-stoichiometic hydrides and carbides. They burn in oxygen to give sesquioxides M_2O_3 (except Ce which gives CeO_3). Their ionic oxides react with water to form insoluble hydroxides. The oxides and hydroxides being strong base react with CO_2 to form carbonates (M_2CO_3). On burning in sulphur these form sulphides (M_2S_3).

UsesofLanthanoids

- Pyrophoric alloys, known as **Misch metals,** contain lanthanoids about 90-95% (Ce 40.5%, lanthanum andneodymium 44%), iron 4.5%, calcium, carbon and silicon about 10.5% are used in cigarette and gas lighters, flamethrowing tanks, toys, tank andtracer bullets as well asinshells.
- Any alloy containing 30% Misch metals and 1% Zrare used for making parts of jetengines.
- Cerium salts are commonly used as catalyst in petroleum cracking (cerium phosphate), volumetric analysis and as oxidi zingagent (ceric sulphate), indying cotton, in lead accumulators etc,
- Oxides of praseodymium (Pr_2O_3) and neodymium (Nd_2O_4) are used in the preparation of coloured glasses and standard filters.
- Oxides of cerium and thoriumare used in the preparation of gas lamp

mantles.

- Cerium oxide is used to prepare sunglasses as cerium cuts off heat and ultra violet light.

ACT INIDES AND THEIR PROPERTIES

(i) The differentiating electron occupies 5f-sub shell and thus these elements also have three outer most shells not filled to their capacity . These are called act inoidsor actinones.

$_{89}$Ac:......$5f^0,6s^2 6p^6 6d^1,7s^2$

$_{90}$Th:......$5f^1,6s^2 6p^6 6d^1,7s^2$

$_{103}$Lw:....$5f^0,6s^2 6p^6 6d^1,7s^2$

(ii) The electronic configuration of act in oidsis $[Rn]5f^{0-14},6d^{0-2},7s^2$where [Rn] stands for radon core. Like lanthanoids, they are placed together because of similar chemical nature.

(iii) Like lanthanoids contraction, these too show actinoid contraction dueto poor shielding effect of 5f- sub shells. Thus, atomic size of actinoids too decreases gradually from Ac to Lw.

(iv) Actinoids show a range of oxidation states, which is due to comparable energies of 5f, 6d and 7s-orbitals. Tlgeneral oxidation state of actinoids is +3; the elements in the first half of the series show higher oxidationstates.

(v) All these elements are strong reducing agents and are very reactive metals. Actinoids are radioactive and, therefore, it is difficult to study their chemical nature. However, relatively more stable isotopes of these elements beyond uranium have been discovered and the chemistry of these elements has been studied to an extent by using radiotracer techniques.

Like lanthanoids, they react with oxygen, halogens, hydrogens, sulphur and acids.

Uses of Actinoids : Only U, Thhave found applications in nuclear reactions under going nuclear fission to produce nuclear power and nuclear bombs.

Key points

- General electronic configuration of d-block elements is (n- 1) $d^{1-10}ns^{0,1,2}$ and that off-block element is (n-2) $f^{0,1,\ 2\ldots14}(n-1)d^{0,1,2}ns^{2}$
- Their melting and boiling points are high which are attributed to the involvement of (n–1) d electrons resulting in strong metallic bonds.
- Successive ionisation enthalpies do not increase as steeply as in the main group elements with increasing atomic number. Hence, the loss of variable number of electrons from (n –1) d orbitals is not energetically unfavourable.
- Ionisation energies where the electronis removed from half-filled or completely filled orbiatl saree specially large. Hence, $Zn^{3+}$is not formed.
- The metals, in addition to variable oxidation states, they exhibit paramagnetic behaviour, catalytic properties and tendency for the formation of colouredions, interstitial compounds and complexes.
- Reactivity of these elements is calculated as a sum of heat of sublimation, ionization enthal pyas well as heat of hydration.
- The transition elements are sufficiently electro positive to dissolve in mineral acids. Of the first series, with the exception of copper, all the metal sare relatively reactive.
- The transition metals react with a number of non-metals like oxygen, nitrogen, sulphur and halogens to form binary compounds. The first series

transition metal oxides are generally formed from the reaction of metals with oxygen at high temperatures.

- These oxides dissolve in acids and bases to for moxo metallic salts.
- The two series of inner transition elements, lanthanoids and actinoids constitute the f-block of the periodictable. With the successive filling of the inner orbitals, 4f, there is a gradual decrease in the atomic and ionicsizes of these metals along the series (lanthanoid contraction). This has far reaching consequences in the chemistry of the elements succeeding them.
- Lanthanum and all the lanthanoids are rather soft white metals. They react easily with water to give solutions giving +3 ions. The principal oxidation state is +3, although +4 and +2 oxidation states are also exhibited by some occasionally.