

Chapter - 08

D & F Block Elements

LECTURE 01

General introduction:-

The d-block of the periodic table contains the elements of the group 3-12 in which the d-orbitals are progressively filled. These elements have their properties which are intermediate between those of S and P block elements, thus are transition elements. The elements constituting the f-block are those in which the 4f and 5f orbitals are progressively filled. These elements are the members of group 3. These elements are also called inner transition elements or metals.

In the periodic table, there are four transition series of elements corresponding to the filling of 3d, 4d, 5d, and 6d sub levels in the 4th, 5th, 6th, and 7th periods.

- (i) First transition series or 3d series consists of 10 elements of the 4th period: Sc (At. No=21), Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn (At. No = 30)
- (ii) Second transition series or 4d series consists of 10 elements of the 5th period: Y (At. No=39), Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, and Cd (At No. = 48)
- (iii) The third transition series or 5d series consists of 10 elements of the 6th period. La (At. No. = 57, Hf (72), Ta, W, Re, Os, Ir, Pt, Au, and Hg (At No = 80)
- (iv) The fourth transition series or 6d series starts with Ac (89) followed by elements with atomic no. 104 onwards.

A transition element is defined as the one which has incompletely filled d orbitals in its ground state or any one of its oxidation states. Zn, Cd, and Hg of group 12 have d¹⁰ configuration in their ground state as well as in their common oxidation states and hence are not regarded as transition metals. However, being the end members of the transition series they are included in transition metals.

Various precious metals such as Ag, Au, Pt, Fe, Cu, and Ti form part of the transition metals.

The Transition Elements (d-Block)

1. Position in the periodic table: The d-block occupies the middle position of S- and P-blocks in the periodic table. The properties of d-block elements are in a transition in between S- and P-blocks elements, therefore these are also called transition elements. The d-orbitals of the

penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition series i.e. 3d, 4d, and 5d. The 6d series is incomplete.

2. Electronic configurations of the d-block elements:

The general electronic configuration is $(n - 1) d^{1-10} ns^{1-2}$. The (n-1) stands for the penultimate shell. This configuration has several exceptions because of very little energy difference between (n-1)d and ns orbitals. Further half and filled orbitals are very stable. For example, the electronic configurations of Cr and Cu are $4s^1 3d^5$ and $4s^1 3d^{10}$ respectively instead of $4s^2 3d^4$ and $4s^2 3d^9$.

The electronic configurations of Zn, Cd and Hg are $4s^2 3d^{10}$, $5s^2 4d^{10}$ and $6s^2 5d^{10}$ respectively. The d orbitals of the transition elements project to the periphery of an atom more than the other orbitals, hence they are more influenced by the surroundings as well as affecting the atoms or molecules surrounding them.

Due to the presence of incompletely filled d orbitals, these elements exhibit similar magnetic properties, variable oxidation states, colored ions, and form complexes. These metals and compounds also exhibit catalytic behavior.

There are greater horizontal similarities in the properties of the transition elements in contrast to the main group elements. This is because all of them contain incompletely filled d-subshell whereas the outer shell electronic configuration remains the same.

3. **Physical properties :**

Except for Zn, Cd, Hg, and Mn all the transition elements display, high tensile strength, ductility, malleability, high thermal and electrical conductivity, metallic luster, and are very hard.

Their melting point and boiling points are high. This is due to the involvement of a greater number of electrons from (n-1) d in addition to the ns electrons in the interatomic metallic bonding. The melting points of these metals rise to a maximum at d^5 except Mn and Tc and fall regularly as the atomic number increases.

They have high enthalpies of atomization. The value is maximum for middle elements in each series. It is due to the presence of strong interatomic interaction. The greater the number of unpaired electrons, the stronger is the resultant bonding. The enthalpies of atomization of Mn is less than Cr. The metals of the second and third series have greater enthalpies of

atomization than the corresponding elements of the first series: this is becoming metal-metal bonding is more frequent in them.

LECTURE 02

Variation of in atomic and ionic sizes of transition metals :

- (i) Generally, the atomic radii of d-block elements in a series decrease with an increase in atomic number but the decrease in atomic size is small after midway. In the 3d series, the metallic radii decrease from Sc to Cr but after that, it remains almost the same. It is because, in the beginning, the atomic radius decreases with the increase in atomic number as the nuclear charge increases whereas the shielding effect of d-electron is small. After midway, as the electrons enter the penultimate shell, the added d-electron shields the outermost electrons more strongly and this effect counterbalance the increase in nuclear charge with an increase in atomic number. As a result in 3d series, atomic radii remain the same after Cr. The same type of behavior is found in the second and third transition series.
- (ii) At the end of the period, there is a slight increase in atomic radii. This is because, near the end, the increased electron-electron repulsion between added electrons in the same orbitals is greater than the attractive forces.
- (iii) The atomic radii increase down the group. But the atomic radii of the second and third transition series are almost the same. This phenomenon is associated with the filling of 4f orbitals before the 5d series of elements begin. The filling of 4f before 5d orbitals results in a regular decrease in atomic radii is called lanthanoid contraction. The net result of the lanthanoid contraction is that the second (4d) and 3rd (5d) transition series exhibit similar radii and have very similar physical and chemical properties.
- (iv) In general ions of the same charge in a given series show a progressive decrease in radius with increasing atomic number. This is because the shielding effect of d electrons are not that effective.
- (v) **Density:** As we move along a transition series from left to right due to an increase in atomic mass and a decrease in atomic volume density increases. Due to the large volume, the density of Zn is less than expected. Among the d-block elements, iridium has the highest density and scandium has the lowest density.

Oxidation states :

- (i) The most common oxidation state of the first-row transition metal is +2 however they show a variety of oxidation states in its compounds.

Oxidation states of 3d transition series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+1	+2
	+3	+3	+3	+3	+3	+3	+3	+2	
+3	+4	+4	+4	+4	+4	+4	+4		
	+5	+5	+5						
		+6	+6	+6					
			+7						

- (ii) The elements which show the greatest no of oxidation states occur in or near the middle of the series. For example Mn. The lesser number of oxidation states at the extreme ends are either due to too few electrons to lose or share or too many d electrons such that fewer orbitals are available to share electrons with others.
- (iii) The maximum oxidation states of reasonable stability in the first transition series are equal to the sum of s and d electrons up to Mn followed by an abrupt decrease in the stability of higher oxidation states.
- (iv) Due to incompletely filled orbitals, transition elements show a wide variety of oxidation states and the oxidation state differs from each other by unity. E.g. +2, +3, +4, +5, etc. oxidation states of non-transition elements normally differ by a unit of two.
- (v) Although in the p-block the lower oxidation states are favored by the heavier members the opposite is true for d-block elements. Thus Cr (VI) in the form of dichromate in acidic medium is a strong oxidizing agent, whereas MoO_3 and WO_3 are not.
- (vi) Low oxidation states are found when a complex compound has ligands capable of π -acceptor character in addition to the σ -bonding. For example in $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$, the oxidation state of nickel and iron is zero.

Ionization enthalpies :

- (i) The first ionization enthalpy of d-block elements are higher than those of s-block elements and are lower than those of p-block elements.
- (ii) The IE_1 value gradually increases with an increase in atomic number along with a given transition series with some exceptions. The increasing ionization enthalpies are due to increased nuclear charge with an increase in atomic number which reduces the size of the atom.

The irregular trend in the 1st ionization enthalpy of 3d metals is because the removal of electrons alters the relative energies of 4s and 3d orbitals. Thus there is reorganization energy accompanying ionization. This results in the release of exchange energy which increases as the number of electrons increases in the d orbital and also from the transference of s-electrons into d-orbitals. Cr has low IE_1 because the loss of one electron gives $3d^5$ (stable configuration).

- (iii) In a given series, the difference in the ionization enthalpies between any two successive d-block elements is very much less than the s-block and p-block elements. This is due to the addition of d electrons in the penultimate shell provides a shielding effect in transition metals.
- (iv) The 1st ionization enthalpy of Zn, Cd, and Hg are however very high because of the filled $(n-1)d^{10}ns^2$ configuration.
- (v) Although 2nd and 3rd I.E. in general, increase along a period, the magnitude of the increase is much higher.
- (vi) THE second I.E. of Cr and Cu are high due to d^5 and d^{10} configuration respectively. 3rd I.E. of Mn is very high due to the d^{10} configuration of Mn^{2+} . THE third I.E. of Fe is very less due to the d^6 configuration of Fe^{2+} .
- (vii) The first ionization enthalpies of 5d elements are higher as compared to those of 3d and 4d elements. This is because of the weak shielding of the nucleus by 4f electrons in 5d elements.

LECTURE 03

Trends in the M^{2+}/M standard electrode potential :

- (i) There are no regular trend in the $E^0 (M^{2+}/M)$ values. This is because their ionization enthalpies (IE_1+IE_2) and sublimation enthalpy do not show any regular trend.
- (ii) The general trend towards less negative E^0 values along the series is due to the general increase in the sum of IE_1 and IE_2 .
- (iii) Copper is the only metal in the series which shows positive E^0 value. This explains why it does not liberate H_2 gas from acids. It reacts only with nitric acid and hot concentrated

H_2SO_4 which are reduced. The reason for the +ve E° value for copper is that the sum of enthalpies of sublimation and ionization is not balanced by hydration enthalpy.

- (iv) The values of E° Mn, Ni, and Zn are more negative than expected from the general trend. This is due to the greater stability of half-filled d-subshell (d^5) in Mn^{2+} and filled d-subshell (d^5) in Mn^{2+} and filled d-subshell (d^{10}) in Zn^{2+} . The exceptional behavior of Ni towards E° value is due to its high negative enthalpy of hydration.

Trends in the M^{3+}/M^{2+} standard electrode potential :

- (i) A very low value for E° ($\text{Sc}^{3+}/\text{Sc}^{2+}$) reflects the stability of Sc^{3+} ion which has a noble gas configuration.
- (ii) The highest value for Zn is due to the high stability of Zn^{2+} ion due to d^{10} configuration.
- (iii) The high value of E° ($\text{Mn}^{3+}/\text{Mn}^{2+}$) shows that Mn^{2+} is very stable due to d^5 configuration.
- (iv) The low value of E° ($\text{Fe}^{3+}/\text{Fe}^{2+}$) is on account of extra stability of Fe^{3+} (d^5) i.e. low third ionization enthalpy of Fe.
- (v) The comparatively low value for V is on account of the stability of V^{2+} ion due to its half-filled t_{2g}^3 configuration.

Trends in the stability of higher oxidation states :

(a) For metal halides :

- (i) The highest oxidation numbers along the series vary from +4 for Ti ($T_1 \times 4$) to +5 for V (VF_5) to +6 for Cr (CrF_6) then to Mn i.e. +7 (MnO_3F). Beyond Mn, no metal shows oxidation no. more than +3, which is only in trihalides, FeX_3 and CoF_3 . The highest oxidation state is generally most stable with fluorine. This is due to either higher lattice energy e.g. in CoF_3 or higher bond enthalpies for the higher covalent compounds e.g. in VF_5 and CrF_6 .
- (ii) Although V directly shows an oxidation state of +5 only in VF_5 , other halides, however, undergo hydrolysis to give oxohalides, VOX_3 in which the oxidation state of V is +5.
- (iii) In the low oxidation states, fluoride is unstable e.g. VX_2 ($X = \text{Cl}, \text{Br}, \text{or I}$) However CuF_2 is known except CuI_2 . Cu^{2+} ion oxidize iodide to iodine. $2\text{Cu}^{2+} + 4\text{I}^- \rightarrow \text{Cu}_2\text{I}_2 + \text{I}_2$ Many copper (I) compounds are unstable in aqueous solutions and undergo disproportionation $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$. The greater stability of $\text{Cu}^{2+}_{(\text{aq})}$ than $\text{Cu}^+_{(\text{aq})}$ is

due to much more negative enthalpy of hydration for $\text{Cu}^{2+}(\text{aq})$ than $\text{Cu}^{+}(\text{aq})$, which more than compensates the 2nd I.E. of Cu.

(b) For metal oxides:-

Oxygen stabilizes the highest oxidation states more than fluorine.

(i) The highest oxidation state in the oxide is the same as that of group number up to group 7 (Sc_2O_3 to Mn_2O_7).

(ii) Beyond group 7, the maximum oxidation state is +3 in (Fe_2O_3), ferrates, $(\text{FeO}_4)^{2-}$ are unstable and readily decompose to Fe_2O_3 and O_2 .

(iii) Besides the oxides, higher oxidation states are also found in oxocations and oxoanions. E.g. V(V) in VO_2^+ , V(IV) in VO^{2+} , Ti(IV) in TiO^{2+} , Mn(VII) in MnO_4^- , Cr(VI) in CrO_4^{2-} , etc.

(iv) Oxygen stabilizes the higher oxidation state more than fluorine, e.g. highest fluoride of Mn is MnF_4 , whereas the highest oxide is Mn_2O_7 . The reason for this is the ability of oxygen to form multiple bonds with the metal atoms.

LECTURE 04

Chemical reactivity and E° values.

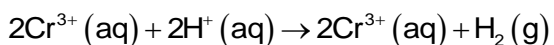
(i) The metals of the first transition series (except Cu) are relatively more reactive than the other series. Thus they are oxidized by H^+ ions but the rate is slow e.g. Ti and V are passive to dilute non-oxidizing acids at room temp.

(ii) More negative $E^\circ(\text{M}^{2+}/\text{M})$ than expected for Mn, Ni and Zn show greater stability for Mn^{2+} , Ni^{2+} and Zn^{2+}

(iii) Less negative E° values for (M^{2+}/M) along the series indicate a decreasing tendency to form a divalent cation.

(iv) E° value for the redox couple $\text{M}^{3+}/\text{M}^{2+}$ indicates that Mn^{3+} and Co^{3+} ions are the strongest oxidizing agents in aqueous solution. Whereas Ti^{2+} , V^{2+} and Cr^{2+} are strongest reducing

agents and can liberate hydrogen from a dilute acid e.g.



Magnetic Properties :

Based on behavior in a magnetic field, substances are classified as paramagnetic, diamagnetic, and ferromagnetic. Those substances which are attracted by the applied magnetic field are called paramagnetic whereas those which are repelled by the magnetic field are called diamagnetic. Substances that are very strongly attracted by the applied magnetic field are called ferromagnetic. Thus ferromagnetism is an extreme case of paramagnetism.

Most of the transition metal ions and their compounds are paramagnetic due to the presence of unpaired electrons in the (n-1)d orbitals. The transition elements which have paired electrons are diamagnetic.

As the number of unpaired electrons increases, the magnetic moment and hence paramagnetic character also increases. The magnetic moment is calculated from the spin only formula, $\mu = \sqrt{n(n+2)}\text{B.M.}$ where n is the number of unpaired electrons and B.M. stand for Bohr magneton.

Formation of Coloured ions :

When an electron from a lower energy d orbital is excited to a higher energy d orbital (d-d transition), the energy of excitation corresponds to the frequency of light absorbed. This frequency generally lies in the visible region. The color observed corresponds to the complementary color of the light absorbed. The frequency of light absorbed is determined by the nature of the ligand.

Formation of complex compounds: Complex compounds are those in which the metal ions bind several anions or neutral molecules giving complex species. A few examples are $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{PtCl}_4]^{2-}$, etc. Transition metals form a large number of complex compounds. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges, and the availability of d orbitals for bond formation.

Catalytic properties: The transition metals and their compounds are known for their catalytic activity. This activity is due to their ability to adopt multiple oxidation states and to form

complexes. Some examples are V_2O_5 , finely divided Fe, Ni, Co, etc. catalyst increases the rate of reaction by increasing the concentration of reactants at the catalyst surface and by lowering the activation energy.

Formation of Interstitial compounds :

Interstitial compounds are those which are formed when small atoms like H, C, or N are trapped inside the crystal lattices of metals. They are usually non-stoichiometric are neither ionic nor covalent. For example $Mn_4N, Fe_3H, VH_{0.56}$ etc. The principal physical and chemical properties are

- (i) They have high melting points, higher than those of pure metals.
- (ii) They are very hard like some borides.
- (iii) They retain metallic conductivity.
- (iv) They are chemically inert.

Alloy Formation :

An alloy is a homogeneous mixture of metals in their molten state. Alloys are formed by atoms with metallic radii that are within about 15 percent of each other. Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. Alloys are hard and have often high melting points. Ex: Brass (Cu-Zn), Bronze (Cu-Sn), etc.

LECTURE 05

Some Important compounds of transition elements :

Oxides and oxoanions of metals :

These oxides are generally formed by the reaction of metals with oxygen at high temperatures.

All the metals except scandium form MO oxides which are ionic.

As the oxidation number of a metal increases, ionic character decreases.

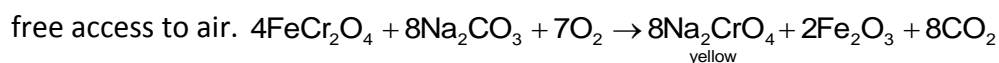
Ex: Mn_2O_7 is a covalent green oil, CrO_3, V_2O_5 , and higher oxides are acidic.

Potassium dichromate ($K_2Cr_2O_7$) :

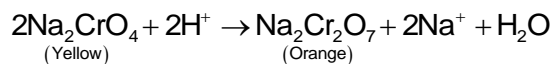
It is used in the leather industry and as an oxidant for the preparation of many azo compounds.

Preparation:

It is prepared by the fusion of chromite ore $[\text{FeCr}_2\text{O}_4]$ with sodium or potassium carbonate in

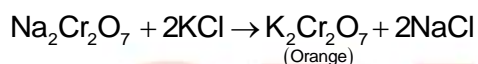


Sodium chromate (yellow) is filtered and acidified H_2SO_4 to give a solution from which orange $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ can be crystallized.

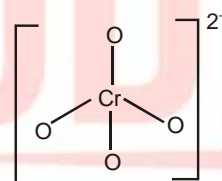


$\text{Na}_2\text{Cr}_2\text{O}_7$ is more soluble than $\text{K}_2\text{Cr}_2\text{O}_7$.

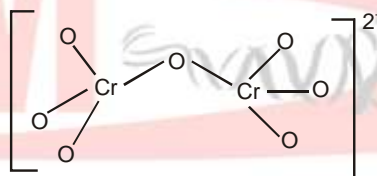
The latter is therefore prepared by using KCl



The chromates and dichromates are inter-convertible in aqueous solution depending upon the pH of the solution :

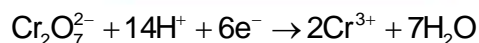


Chromate ion
(tetrahedral)

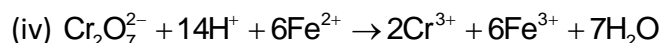
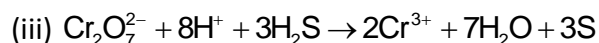
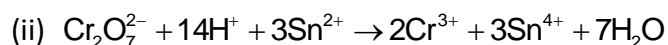
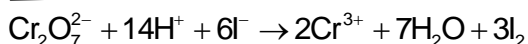
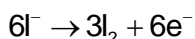
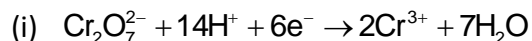


Dichromate ion

Sodium and potassium dichromates are strong oxidizing agents. $\text{K}_2\text{Cr}_2\text{O}_7$ is used in volumetric analysis. In acidic solution, its oxidizing action can be represented as



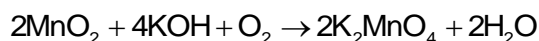
It can oxidize iodide to iodine. Sulphides to sulphur, tin (II) to tin (IV) and iron (II) to iron (III)



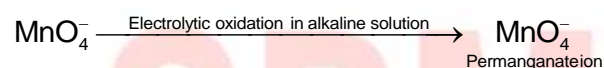
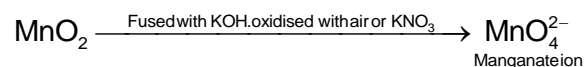
Potassium Permanganate (KMnO₄):

It is prepared by fusion of MnO₂ with a metal hydroxide and oxidizing agent like KNO₃.

This produces the dark green K₂MnO₄ which disproportionates in a neutral or acidic solution to give permanganate.



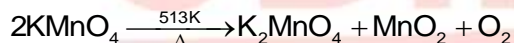
Commercially it is prepared by the alkaline oxidative fusion of MnO₂ followed by the electrolytic oxidation of manganate (VI)



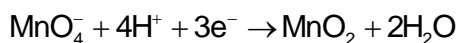
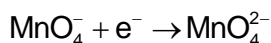
In the laboratory, Mn(II) ion salt is oxidized by peroxodisulphate to permanganate.



KMnO₄ forms dark purple crystal which is isostructural with KClO₄.

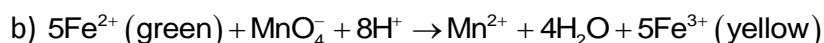
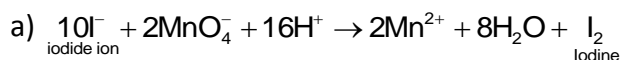


We can represent the reduction of permanganate to manganate, MnO₂ and Mn(II) salt by half-reactions.



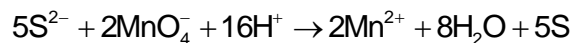
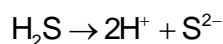
A few important oxidizing reactions KMnO₄ are given below.

1. In acid solutions :

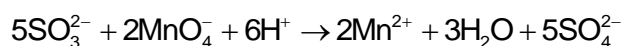




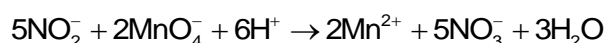
d) Hydrogen sulphide is oxidized to sulphur



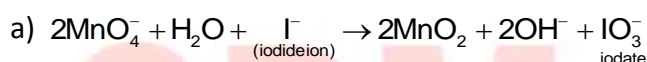
e) Sulphurous acid or sulphite is oxidized to sulphate or sulphuric acid.



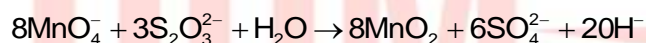
f) Nitrite is oxidized to nitrate :



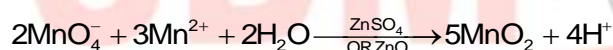
2. In neutral or faintly alkaline solutions :



b) Thiosulphate is oxidized to sulphate :



c) Manganous salt is oxidized to MnO_2



Permanganate titrations in presence of HCl are not used because HCl is oxidized to Cl_2 .

Uses : (i) It is used in the volumetric analysis (ii) It is used as an oxidizing agent (iii) It is used for bleaching of wool, cotton, silk and the decolorization of oils.

LECTURE 06

The Inner Transition Elements (f-Block):

The f-block elements consist of the two series, Lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium)

The Lanthanoids (At.No. 57-71):

Electronic Configurations :

Atoms of these elements have an electronic configuration with $6s^2$ common but with variable occupancy of 4f level. However, the electronic configuration of all the trip positive ions (the most stable state of lanthanoids) are of the form $4f^n$ ($n = 1$ to 14)

Atomic and ionic sizes :

The overall decrease in atomic and ionic radii from lanthanum to lutetium with an increase in atomic number is called lanthanoid contraction. The decrease in ionic size (M^{3+} ion) is quite regular but the decrease in atomic size is not regular. The decrease in size is due to the poor shielding of 4f electrons than d electrons.

Due to lanthanoid contraction, the radii of the members of the third transition series to be very similar to those of the corresponding members of the 2nd series. The almost identical radii of Zn and Hf, a consequence of the lanthanoid contraction account for their occurrence together in nature and for the difficulty faced in their separation.

Oxidation states: In the lanthanoids, La (III) and Ln (III) compounds are the predominant species. However, occasionally +2 and +4 ions in solution or solid compounds are also obtained. This irregularity arises mainly from the extra stability of empty, half-filled, or filled f subshell. Thus Ce^{+4} is favored by its noble gas configuration. Pr, Nd, Tb, Dy also exhibit +4 oxidation state only in their oxides. Eu^{2+} is a strong reducing agent changing to the common +3 state, $Yb^{2+} (f^{14})$ is a reductant, and $Tb^{4+} (f^7)$ acts as an oxidant.

General characteristics :

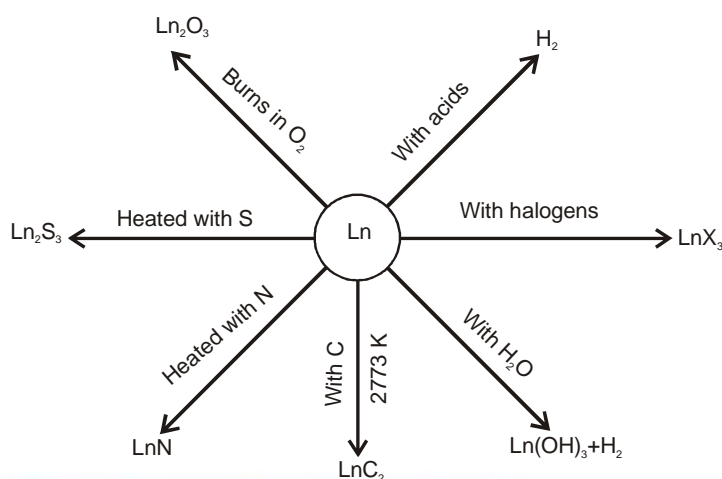
All the lanthanoids are silvery-white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number. They have a typical metallic structure and are good conductors of heat and electricity.

Many trivalent lanthanoid ions are colored both in solid-state and in aqueous solution due to the presence of unpaired electrons in an f subshell. $La^{3+} (4f^0)$ and $Lu^{3+} (4f^{14})$ are colorless. The lanthanoid ions are paramagnetic except $La^{3+} (f^0)$, $Ce^{4+} (f^0)$, $Yb^{2+} (f^{14})$ and $Lu^{3+} (f^{14})$.

Chemical behavior :

The earlier members of the series are quite reactive similar to calcium but, with increasing atomic number, they behave more like aluminum. The metals combine with hydrogen when gently heated. The carbides Ln_3C , Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon. They liberate hydrogen from dilute acids and burn in halogens to form halides. They

form oxides M_2O_3 and hydroxides $M(OH)_3$. They are basically like alkaline metal oxides and hydroxides.



Uses :

- Lanthanoids are used for the production of alloy steels for plates and pipes. Mischmetal a well-known alloy consists of (~95%) lanthanoid metal and iron (~5%) and traces of S, C, Ca, and Al. This alloy is used in Mg-based alloy to produce bullets, shells, and lighter flint.
- Mixed oxides of lanthanoids are used as catalysts in petroleum cracking.
- Some Ln oxides are used in television screens.

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LECTURE 07

The Actinoids: The actinoids include the fourteen elements from Th to Lr (atomic number 90 to 103) excluding actinium ($Z=89$). The actinoids are radioactive elements and the earlier members have long half-lives, the latter ones have very few half-lives, which render their study more difficult.

Electronic configurations :

- All the actinoids have a common $7s^2$ configuration and variable occupancy of 5f and 6d subshells.
- The 14 electrons are being added into 5f, except in thorium ($Z=90$) and after the filling of 5f continues till lawrencium ($Z = 103$).

(iii) The irregularities in the electronic configuration of actinoids are related to the stability of f^0 , f^7 , and f^{14} configuration.

(iv) 5f orbitals are less deeply buried than 4f. Hence 5f electrons can participate in bonding to a greater extent.

Ionic sizes:

There is a gradual decrease in the size of atoms or M^{3+} ions across the series with an increase in atomic number, which is called actinoid contraction. Actinoid contraction is greater than lanthanoid contraction due to the very poor shielding effect of 5f electrons.

Oxidation states :

The common oxidation state of these elements is +3, Neptunium (Np) and plutonium (Pu) can exhibit +3 to +7 oxidation state.

Unlike lanthanoids, actinoids show a large number of oxidation states. This is because of the very small energy gap between 5f, 6d, and 7s subshells.

General characteristics of Actinoids :

- (i) Actinoids are metals with a silvery appearance. However, actinoid cations are colored due to the presence of unpaired electrons in an f subshell.
- (ii) They have a high melting point, boiling point.
- (iii) They have lower I.E. than lanthanoids.
- (iv) They are strongly paramagnetic.
- (v) Chemical behavior:
 - (a) They are highly reactive metals in the finely divided state.
 - (b) They react with boiling water to give a mixture of oxides and hydride.
 - (c) They can react with non-metals.
 - (d) All these metals are attacked by hydrochloric acid but HNO_3 can form a protective layer on their surface.
 - (e) Alkalies have no action on them.

Uses of Actinoids :

- (i) Thorium is used in atomic reactors and the treatment of cancer.
- (ii) Uranium is used as a nuclear fuel. Its salts are used in the glass industry (green color), the textile industry, ceramic industry, and in medicines.
- (iii) Plutonium is used as a fuel for atomic reactors as well as for making atomic bombs.

Comparison of Lanthanoids and Actinoids:-**Similarities :**

- (i) Both show mainly an oxidation state of +3.
- (ii) Both are electropositive and very reactive.
- (iii) Both exhibit magnetic properties.
- (iv) Actinoids exhibit actinoid contraction like lanthanoid contraction shown by lanthanoids.

Differences:

	Lanthanoids		Actinoids
(i)	They show +2, +3 and +4 oxidation states only	(i)	They show +3, +4, +5, +6 and +7 oxidation state also.
(ii)	They have less tendency towards complex formation.	(ii)	They have more tendency towards complex formation.
(iii)	Lanthanoid oxide and hydroxides are less basic	(iii)	Actinoid oxide and hydroxides are more basic.
(iv)	Except promethium, they are non radioactive.	(iv)	They are radioactive.

Questions for practice(LECT-1):

1. On what ground can you say that Sc is a transition element but Zn is not?
2. The silver metal atom has filled d orbitals in its ground state. How can you say that it is a transition element?
3. Why the metals of the second and third transition series have greater enthalpies of atomization than the corresponding elements of the first series?

4. Why there are greater horizontal similarities in the properties of the transition elements in contrast to the main group elements?
5. Write down the electronic configuration of (i) Cr^{3+} (ii) Cu^+ (iii) Mn^{2+} (iv) Ce^{4+}
6. Zn is soft whereas Cr is hard. Give reason.
7. The enthalpies of the atomization of transition metals are quite high. Explain why?
8. Why d-block elements are called transition elements?

Questions for Practice (LECT-2)

1. Name a transition element which does not exhibit variable oxidation states.
2. Which of the 3d series of the transition metals exhibits the largest number of oxidation states and why?
3. Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state?
4. To what extent does the electronic configuration decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples.
5. Name the oxometal anions of the 1st series of the transition metals in which the metal exhibits the oxidation state equal to its group number.
6. In what way the electronic configuration of the transition elements different from that of the non-transition elements?
7. How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with an example.
8. Why the 1st I.E. of 5d elements are higher as compared to those of 3d and 4d elements?
9. The corresponding members of the second (4d) and third (5d) transition series exhibit similar atomic radii. Explain why?
10. Why at the end of the transition series, there is a slight increase in the atomic radii?

Questions for Practice (LECT-3)

1. Why is Cr^{2+} reducing and Mn^{3+} oxidizing when both have d^4 configuration?
2. The $E^\circ (\text{M}^{2+} / \text{M})$ value of Cu is +ve. What is possibly the reason for this?
3. How would you account for the increasing oxidizing power in the series $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$?
4. How would you account for the irregular variation of ionization enthalpies (first and second) in the first series of the transition elements?

5. Why is the E° value for the Mn^{3+}/Mn^{2+} couple much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+} ? Explain.
6. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?
7. Which is a stronger reducing agent Cr^{2+} or Fe^{2+} and why?
8. How would you account for the following?
 - (i) Out of the d^4 species, Cr^{2+} is strongly reducing while manganese (III) is strongly oxidizing.
 - (ii) Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents, it is easily oxidized.
 - (iii) The d^1 configuration is very unstable in ions.
9. What is meant by the disproportionate of an oxidation state? Give an example.
10. Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

Questions for Practice (LECT-4)

1. Calculate the 'spin only' magnetic moment of M^{2+} (aq) ion ($Z = 27$).
2. What are interstitial compounds? Why such compounds well known for transition metals?
3. What are alloys? Name an important alloy that contains some of the lanthanide metal. Mention its uses.
4. Explain giving reasons:
 - (i) Transition metals and many of their compounds show paramagnetic behavior.
 - (ii) The transition metals generally form colored compounds.
 - (iii) Transition metals and their many compounds act as a good catalyst.
5. Zn^{2+} salts are white while Cu^{2+} salts are colored why?
6. Which divalent metal ion has maximum paramagnetic character among the 1st transition metals? And why?
7. In the following ions, Mn^{3+} , V^{3+} ($Z = 23$), Cr^{3+} and Ti^{4+} ($Z = 22$)
 - (i) Which ion is most stable in aqueous solution.
 - (ii) Which ion is the strongest oxidizing agent?
 - (iii) Which ion is colorless?

(iv) Which ion has the maximum number of unpaired electrons?

8. Give reasons for the following :

(i) E° values of Mn, Ni, and Zn are more negative than expected.

(ii) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is colored while $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is colorless.

Questions for Practice (LECT-5)

1. Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?
2. Describe the oxidizing action of potassium dichromate and write the ionic equations for its reaction with (i) iodide (ii) iron (II) solution and (iii) H_2S
3. Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron (II) ions (ii) SO_2 and (iii) oxalic acid?
4. Draw the structure of chromate and dichromate ions.
5. Complete the following equations :
 - (i) $2\text{MnO}_4^- + 6\text{H}^+ + 5\text{SO}_3^{2-} \rightarrow$
 - (ii) $2\text{MnO}_4^- + 6\text{H}^+ + 5\text{NO}_2^- \rightarrow$
 - (iii) $\text{KMnO}_4 \xrightarrow{\Delta}$
6. Write chemical equations for the following reactions in neutral or alkaline solutions.
 - (i) Oxidation of iodide to iodate by MnO_4^- ion.
 - (ii) Oxidation of Thiosulphate to sulphate by MnO_4^- ion
 - (iii) Oxidation of manganous salt to MnO_2 by MnO_4^- ion.
7. Draw the structure of manganate and permanganate ion.
8. Complete the following equations :
 - (i) $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \rightarrow$
 - (ii) $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow$

Questions for Practice (LECT-6)

1. Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.
2. Name an alloy that contains some of the lanthanoid metals. Mention its uses.

3. Use Hunt's rule to derive the electronic configuration of Ce^{3+} ion, and calculate its magnetic moment.
4. 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.
5. What is lanthanoid contraction? Write the common oxidation state of lanthanoids.
6. Sm^{2+} , Eu^{2+} and Yb^{2+} ions in solutions are good reducing agents but in an aqueous solution of Ce^{4+} is a good oxidizing agent. Why?
7. Zr belongs to 4d and Hf belongs to the 5d transition series but it is quite difficult to separate them. Why?
8. What are the consequences of lanthanoid contraction?
9. Why La^{3+} and Ce^{4+} ions are not paramagnetic nature.
10. Many trivalent lanthanoid ions are colored both in solid-state and in aqueous solution why?

Questions for Practice (LECT-7)

1. Actinoid contraction is greater from element to element than lanthanoid contraction why?
2. The chemistry of actinoids is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements or write any two reasons.
3. Which is the last element in the series of the actinoids? Write all its possible oxidation states.
4. What are the inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements: 29, 59, 74, 95, 102, and 104.
5. Compare the chemistry of actinoids with that of lanthanoids concerning
 - (i) Electronic configuration
 - (ii) Oxidation states and
 - (iii) Chemical reactivity
6. Actinoids show a large number of oxidation states as compared to lanthanoids. Why?
7. Write some common uses of actinoids.