

d -Block Elements

1. TRANSITION ELEMENTS AND COMPLEXES

- * In the long form of periodic table elements are classified based on electronic configuration. The elements which are classified between 's' and 'p' block are 'd' block elements or Transition elements. In these elements the differentiating electron enters in the 'd' orbitals of penultimate shell.
- * General configuration for 'd' block elements is $ns^{1-2} (n-1)d^{1-10}$. i.e., in 'd' block elements the valence shell has constant number of electrons whereas the number of electrons in penultimate shell go on increasing.
- * Elements which have at least one unpaired electron in their 'd' orbital in atomic or any oxidation state are called as Transition elements. Thus all transition elements are 'd' block elements but all 'd' block elements may not be transition elements or the elements having incompletely filled 'd' orbitals are called as transition elements.
- * Transition elements are classified between 's' and 'p' blocks from fourth period onwards. Series of transition elements are four
- * **1st Series** - They are classified in fourth period and are called as '3d' series of elements. Their atomic numbers are 21(Sc) to 30 (Zn).
- * **2nd Series**- They are classified in fifth period and are called as '4d' series of elements. Their atomic numbers are 39(Y) to 48(Cd).
- * **3rd series**- They are classified in sixth period and are called as '5d' series of elements. Their atomic numbers are 57(La), 72(Hf) to 80(Hg)
- * **4th Series** - They are classified in the seventh period and are called as '6d' series of elements. This is an incomplete series. Their atomic numbers are 89(Ac), 104(Ku) to 112 (Uub).

- * Electronic configuration of first series of transition elements.

Atomic number	Element	Symbol	Electronic configuration
21.	Scandium	Sc	[Ar] $4s^2 3d^1$
22.	Titanium	Ti	[Ar] $4s^2 3d^2$
23.	Vanadium	V	[Ar] $4s^2 3d^3$
24.	Chromium	Cr	[Ar] $4s^1 3d^5$
25.	Manganese	Mn	[Ar] $4s^2 3d^5$
26.	Iron	Fe	[Ar] $4s^2 3d^6$
27.	Cobalt	Co	[Ar] $4s^2 3d^7$
28.	Nickel	Ni	[Ar] $4s^2 3d^8$
29.	Copper	Cu	[Ar] $4s^1 3d^{10}$
30.	Zinc	Zn	[Ar] $4s^2 3d^{10}$

- * Chromium and copper are elements having exceptional electronic configurations of [Ar] $4s^1 3d^5$ and [Ar] $4s^1 3d^{10}$ instead of [Ar] $4s^2 3d^4$ and [Ar] $4s^2 3d^9$

- * Zn (30) is [Ar] $4s^2 3d^{10}$
Cd (48) is [Kr] $5s^2 4d^{10}$
Hg (80) is [Xe] $6s^2 4f^{14} 5d^{10}$

These three elements do not have any unpaired electrons in their 'd' orbitals in atomic as well as in ionic states. Therefore they are only classified as 'd' block elements and not as transition elements. Copper, Silver and Gold, the elements of IB group i.e., coinage metals, have $ns^1 (n-1)d^{10}$ configuration. They are transition elements as in their higher oxidation state they have an unpaired electron in their 'd' orbitals.

2. GENERAL PROPERTIES OF D-BLOCK ELEMENTS

- * All the elements of '3d' series are good reducing agents except copper.
- * In general the reactivity of transition elements is less. Their reactivity decreases with increase in atomic number. The atomic radii of transition elements decrease by negligible amounts due to the shielding of valence shell electrons, provided by electrons of 'd' orbitals of penultimate shell.
- * The ionisation potential of transition elements increase by negligible amounts due to shielding effect.

2.1 Metallic Character

- * All the d-block elements are metals as the numbers of electrons in the outer most shell are one or two.
- * They are hard malleable and ductile. IB group elements Cu, Ag and Au are most ductile and soft.
- * These are good conductor of heat and electricity (due to free e-) IB gp. elements are most conductive in nature. Their order of conductivity is

$$\text{Ag} > \text{Cu} > \text{Au} > \text{Al}.$$

2.2 Atomic size

- * Atomic and ionic radii of d-block elements is smaller than s-block elements
- * Atomic radii depends on effective nuclear charge (Z_{eff}) and screening effect (SE).
- * In 3d series
 $\text{Sc} \rightarrow \text{Cr}$ ($Z_{\text{eff}} > \text{SE}$) \therefore radius decreases
 $\text{Mn} \rightarrow \text{Ni}$ ($Z_{\text{eff}} = \text{SE}$) \therefore radius remains constant
 $\text{Cu} \rightarrow \text{Zn}$ ($Z_{\text{eff}} < \text{SE}$) \therefore radius increases
- * In dipositive ions of 3d series Cu^{+2} is the smallest in size.
- * The elements of 4d and 5d series belongs to a particular group have almost same atomic radii. This is due to Lanthanide contraction. e.g. Zr \square Hf, Tc \square Re, Nb \square Ta, Ru \square Os etc.
- * In d-block elements
 Largest atomic radii - La
 Smallest atomic radii - Ni
- * In IIIB group order of atomic radii is
 $\text{Sc} < \text{Y} < \text{La}$ (No lanthanide contraction)

2.3 Density

- * The atomic volume of the transition elements are low compared with s-block, so their density is comparatively high ($D = M/V$)
- * Except Sc, Y and Ti, all the d-block elements have density greater than 5 gm cm^{-3}
- * Os (22.57 gm cm^{-3}) and Ir (22.61 gm cm^{-3}) have highest density.
- * In all the groups there is normal increase in density from 3d to 4d series, and from 4d to 5d it increases just double it is due to lanthanide contraction. $\text{Ti} < \text{Zr} \ll \text{Hf}$
- * In 3d series
 $\text{Sc} \rightarrow \text{Cr}$ density increases
 $\text{Mn, Fe, Co, Ni} \rightarrow$ almost constant
 $\text{Cu} \rightarrow \text{Zn}$ decreases
- * In 3d series highest density – Cu
 lowest density – Sc
- * Some important orders of density
 $\text{Fe} < \text{Ni} < \text{Cu}$
 $\text{Fe} < \text{Cu} < \text{Au}$
 $\text{Fe} < \text{Hg} < \text{Au}$

2.4 Melting and boiling points

- * M.P. and b. p. of d-block > s-block (the reason is stronger metallic bond and presence of covalent bond formed by unpaired d-electrons.)
- * In Zn, Cd, and Hg there is no unpaired electron present in d-orbital, hence due to absence of covalent bond, their m.p. and b.p. are very low. (Volatile metals Zn, Cd, Hg)
- * In 3d series
Sc → Cr m.p. b.p increases
Mn → Zn m.p. b.p decreases
- * Mn and Tc possess comparatively low m.p., it due to stable configuration' (Half filled)
- * Lowest mp Hg - 38°C
Highest mp. W □ 3400°C
- * **Characteristic properties of transition elements are**
 - (a) Variable oxidation state
 - (b) Coloured ions
 - (c) Paramagnetic properties
 - (d) Catalytic properties
 - (e) Formation of alloys
 - (f) Formation of interstitial compounds and
 - (g) Formation of complexes.

(a) Variable valency or variable oxidation states:

They exhibit variable valency due to involvement of (ns) and (n-1)d electrons in bonding. This is due to less energy difference between these electrons.

- * The oxidation states of all transition elements of '3d' series are as follows

Sc	[Ar] 4s ² 3d ¹								
Ti	[Ar] 4s ² 3d ²	(+2)	+3	+4					
V	[Ar] 4s ² 3d ³	+2	+3	+4	+5				
Cr	[Ar] 4s ¹ 3d ⁵	(+1)	+2	+3	(+4)	(+5)	+6		
Mn	[Ar] 4s ² 3d ⁵	+2	+3	+4	(+5)	(+6)	+7		
Fe	[Ar] 4s ² 3d ⁶	+2	+3	(+4)	(+5)	(+6)			
Co	[Ar] 4s ² 3d ⁷	+2	+3	+4					
Ni	[Ar] 4s ² 3d ⁸	+2	(+3)	(+4)					
Cu	[Ar] 4s ¹ 3d ¹⁰	+1	+2						

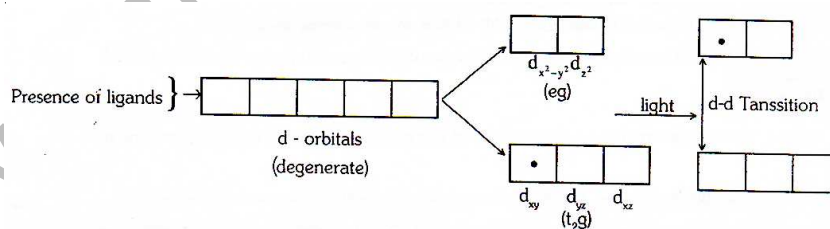
Oxidation States in brackets is/are unstable.

- * Highest oxidation state of transition elements can be calculated by = n + 2 (n = no. of unpaired e-) (It is not applied for Cr and Cu)
- * The transition metal ions having stable configuration are stable
Metal ions of '3d' series having 3d⁰ configuration Sc⁺³, Ti⁺⁴ and V⁺⁵ etc are stable.
Transition metal ions having 3d⁵ configuration are stable like Mn⁺², Fe⁺³
In aqueous medium Cr⁺³ is stable.
Co⁺² and Ni⁺² are stable.
- * Transition metal ion with 3d¹⁰ configuration which is stable is Cu⁺¹. In aqueous medium Cu⁺² is more stable than Cu⁺¹.
- * Most common oxidation state among the transition elements is +2.
- * Highest oxidation state shown by transition elements of '4d' and '5d' series is +8. The elements showing this oxidation state are Ruthenium (44) and Osmium (76).

- * The common oxidation state shown by elements of IIB i.e., Sc, Y, La and Ac is +3 as their divalent compounds are highly unstable.
- * In lower oxidation state transition elements form ionic compounds and in higher oxidation state their compounds are covalent.
e.g. in chromate ion CrO_4^{-2} , the bonds between Cr and O are covalent.
- * Generally higher oxidation states are exhibited in the compounds which are formed with highly electronegative elements like O and F.
- * They also shows zero oxidation state in their carbonyl compounds like $\text{Ni}(\text{CO})_4$
- * Usually transition metal ions in their lower oxidation state act as reducing agents and in higher oxidation state they are oxidising agents.
e.g. – Ti^{+2} , V^{+2} , Fe^{+2} , Co^{+2} etc are reducing agents
 Cr^{+6} , Mn^{+7} , Mn^{+4} , Mn^{+5} , Mn^{+6} etc are oxidising agents.

2.5 Colour Property:

- * Most of the transition metal ions exhibit colour property. This is due to the presence of unpaired electrons in their 'd' orbitals. They require less amount of energy to undergo excitation of electrons. Hence they absorb visible region of light exhibiting colour.
 $\text{Ti}^{+2}[\text{Ar}]3d^2$, $\text{V}^{+2}[\text{Ar}]3d^3$ etc.
These are having unpaired electrons in their 'd' orbitals therefore they are coloured.
- * Transition metal ions which do not have any unpaired electrons in their 'd' orbitals like $3d^0$ and $3d^{10}$ configurations, do not exhibit any colour property.
e.g., $\text{Sc}^{+3}[\text{Ar}]3d^0$, $\text{Cu}^{+1}[\text{Ar}]3d^{10}$, $\text{Ti}^{+4}[\text{Ar}]3d^0$ etc are colourless ions.
- * A transition metal ion absorbs a part of visible region of light and emits rest of the six colours, the combination of which is the colour of emitted light. The colour of metal ion is the colour of the emitted light.
- * In transition metal ion the 'd' orbitals split into lower energy set t_{2g} orbitals and higher energy set eg orbitals. The electrons from t_{2g} set get excited to higher energy set i.e., eg set. This excitation of electrons is called as 'd-d' transition. As d-d transition requires less amount of energy they absorb visible region of light. Due to this 'd-d' transition the transition metal ions exhibit colour property.
Lower energy set = t_{2g}
Higher energy set = eg.



- * KMnO_4 (dark pink), $\text{K}_2\text{Cr}_2\text{O}_7$ (orange) having d^0 configuration are coloured due to charge transfer spectrum.

Some of the coloured metal ions are as follows :

Ti^{+3} -	Purple	Cr^{+3}	Green
Mn^{+2} -	Light pink	Fe^{+2} -	Pale green
Fe^{+3} -	yellow	Co^{+2} -	Blue
Ni^{+2}	green	Cu^{+2} -	Blue

2.6 Magnetic properties

- * Matter, in general is associated with magnetic properties. Majority of substances are either paramagnetic or diamagnetic. A paramagnetic substance is one which is attracted into a magnetic field. Paramagnetism is mainly due to the presence of unpaired electrons in atoms or ions or molecules. Diamagnetic substance is one which is slightly repelled by a magnetic field.

- * $Ti^{+2} [Ar]3d^2$, $Ti^{+3} [Ar]3d^1$, $V^{+2}[Ar]3d^3$, $Cr^{+3}[Ar]3d^3$
As is evident most of the transition metal ions have unpaired electrons in their 'd' orbitals. Hence most of the transition metal ions are paramagnetic in nature. Transition metal ions having $3d^0$ and $3d^{10}$ configuration exhibit diamagnetic nature.
- * An unpaired electron spins and as it is a charged particle, magnetic field is created due to its spinning.
- * Each electron may, in fact, be considered as a micro magnet having a certain value of magnetic moment. The total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons. Thus substances containing unpaired electrons get attracted towards the magnets exhibiting paramagnetic nature.
- * The magnetic moment (μ) created due to spinning of unpaired electrons can be calculated by using

$$\mu = \sqrt{n(n+2)} :$$
 Where 'n' is the number of unpaired electrons in the metal ion.

$$\mu = \text{Magnetic moment in Bohr Magnetons (B.M.)}$$
- * The magnetic moment of diamagnetic substances will be zero.
- * As the number of unpaired electrons increase the magnetic moment created goes on increasing and hence the paramagnetic nature also increases.
- * Transition metal ions having d^5 configuration will have maximum number of unpaired electrons therefore they will be maximum paramagnetic in nature.

2.7 Catalytic Property

- * Transition elements and their compounds exhibit catalytic properties. This is due to their variable valency as well as due to the free valencies on their surface.
- * When transition elements and their compounds are in powdered state, their catalytic properties exhibited will be to a greater extent. This is due to greater surface area available in the powdered state.
- * Transition metals and their compounds exhibiting catalytic properties in various processes are
 - (i) Fe is used in Haber's process for manufacture of NH_3 .
 - (ii) V_2O_5 is used in contact process for H_2SO_4 manufacture
 - (iii) Pt is used in Ostwald's process of nitric acid
 - (iv) Ni is used in hydrogenation of oils
 - (v) $FeSO_4$ is used in oxidation of Benzene with H_2O_2
 - (vi) Cu is used in dehydrogenation of alcohols
 - (vii) $TiCl_4$ is used as catalyst in Vinyl polymerisation.

2.8 Formation of Alloy

- * Transition elements have maximum tendency to form alloys.
- * The reactivity of transition elements is very less and their sizes are almost similar. Due to this a transition metal atom in the Lattice can be easily replaced by other transition metal atom and hence they have maximum tendency to form alloys.
- * In the alloys ratio of component metals is fixed.
- * These are extremely hard and have high M.P.

3. SOME IMPORTANT ALLOY

- | | | | |
|----|---------------|---|----------------------------------|
| 1. | Bronze | - | Cu (75 - 90 %) + Sn (10 - 25 %) |
| 2. | Brass | - | Cu (60 - 80 %) + Zn (20 - 40 %) |
| 3. | Gun metal | - | (Cu + Zn + Sn) (87 : 3 : 10) |
| 4. | German Silver | - | Cu + Zn + Ni (2 : 1 : 1) |
| 5. | Bell metal | - | Cu (80%) + Sn (20%) |
| 6. | Nichrome | - | (Ni + Cr + Fe) |

7.	Alnico	-	(Al, Ni, Co)
8.	Type Metal	-	Pb + Sn + Sb
9.	Alloys of steel		
	(a) Vanadium steel	-	V (0.2 – 1%)
	(b) Chromium steel	-	Cr (2 – 4%)
	(c) Nickel steel	-	Ni (3 – 5%)
	(d) Manganese steel	-	Mn (10 – 18%)
	(e) Stainless steel	-	Cr (12 – 14%) & Ni (2–4%)
	(f) Tunguston steel	-	W (10 – 20%)
	(g) Invar	-	Ni (36%)
10.	14 Carat Gold	-	54% Au + Ag(14 to 30%) + Cu (12 – 28%)
11.	24 Carat Gold	-	100% Au
12.	Solder	-	Pb + Sn
13.	Magnallium	-	Mg (10%) + Al (90%)
14.	Duralumin	-	(Al + Mn + Cu)
15.	Artificial Gold	-	Cu (90%) + Al (10%)
16.	Constantan	-	Cu (60%) + Ni (40%)

3.1 % of Carbon in different type of Iron:

	Name	% of C
1.	Wrought Iron	.1 to .25
2.	Steel	.25 to 2.0
3.	Cast Iron	2.6 to 4.3
4.	Pig Iron	2.3 to 4.6

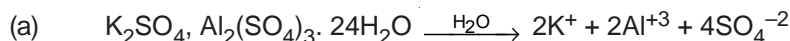
3.2 Formation of Interstitial Compounds

- * Transition elements form interstitial compounds with smaller sized non metal elements like hydrogen, carbon, boron, nitrogen etc. The smaller sized atoms get entrapped in between the interstitial spaces of the metal Lattices.
- * These interstitial compounds are non stoichiometric in nature and hence cannot be given any definite formula.
- * The smaller sized elements are held in interstitial spaces of transition elements by weak Vander Waals forces of attractions.
- * The interstitial compounds have essentially the same chemical properties as the parent metals but they differ in physical properties such as density and hardness.

4. COMPLEX FORMATION

- * Transition metal ions have maximum tendency to form complexes. In the formation of complexes they form coordinate covalent bonds and act as electron pair acceptors.
- * Transition metal ions have smaller size and have high positive charge i.e., high charge density. Due to this they have maximum tendency to accept electrons. They have vacant 'd' orbitals available on them hence they can accept lone pairs of electrons forming coordinate covalent bond.
- * The greater the charge density on the transition metal ion, the greater they have tendency to form complexes. Thus Ti^{+2} to Ni^{+2} the stability of complexes formed goes on increasing.
- * Compounds like NaCl, $Al_2(SO_4)_3$ and K_2SO_4 provide only two types of ions in aqueous solution i.e., cations and anions, are called as simple salts.
- * When two or more simple salt solutions are mixed and then subjected for crystallisation, the crystals which are obtained are of addition compounds.

The addition compound formed may behave in one of the following ways



Common alum

The addition compound which undergoes complete ionisation to form three types of ions i.e., two types of cations and one type of anions or vice versa, is called as double salt. These double salts lose their identity in aqueous solution.



potassium ferrocyanide

Ferrocyanide ion

Addition compound of this type which undergoes partial ionisation to form a complex ion in aqueous solution is called as complex compound or coordination compound. Complexes retain their identity in aqueous solution

4.1 Complex ion –

An aggregate of metal ion with anions cation or neutral molecules is called as complex ion. The metal ion which forms complex ion in combination with anions or neutral molecules is called as central metal ion. Central metal ion acts as an electron pair acceptor and forms coordinate covalent bond

The anions or neutral molecules which combine with central metal ion to form complex ion are called as ligands. They act as electron pair donors or Lewis bases.

4.2 Coordination number

(i) The number of ligands that combine with the central metal ion to form the complex ion is called as coordination number.

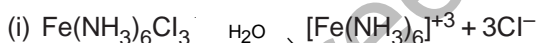
(ii) From every ligand central metal ion accepts lone pair of electrons. Thus the number of lone pair of electrons accepted by the central metal ion in the formation of a complex is called as coordination number.

(iii) The total number of coordinate covalent bonds formed by central metal ion with Ligands is called as coordination number.

4.3 Coordination sphere - Central metal ion and the ligands attached to it, this aggregate which is written in square bracket is called as coordination sphere.

* Werner's Theory of complexes - This was postulated by Alfred Werner in 1893.

The postulates of Werner's Theory of complexes are



Every metal forming a complex exhibits two types of valencies - Primary valency and Secondary Valency. In the above complexes chlorines act as primary valencies and NH_3 acts as secondary valency.

Primary valency is equal to oxidation state of metal ion.

(ii) Primary valency is satisfied by anions whereas secondary valency of the metal ion may be satisfied by anions, neutral molecules or rarely by cations.

(iii) Primary valency is ionisable in nature whereas secondary valency is nonionisable.

(iv) The number of secondary valencies of a metal ion in the complex will remain constant and this is called as coordination number

e.g. Fe^{+2} , Fe^{+3} , Co^{+3} , Pt^{+4} , Cr^{+3} , Ru^{+2} , Os^{+3} have a coordination number of six

Pt^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , Au^{+3} , Hg^{+2} have a coordination number of four.

Ag^{+1} which is an exceptional ion with coordination number of two.

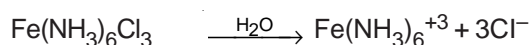
Mo^{+3} has the highest coordination number of eight.

4.4 Shapes and isomerism in complexes

The shape of 6-coordinated complexes can be hexagonal planar or octahedral (more possible). The 6-coordinated complexes can exhibit geometrical or optical isomerism. The shape of 4-coordinated complexes can be square planar (exhibiting geometrical isomerism) or Tetrahedral (exhibiting optical isomerism).

- * Experimental evidence to werner's theory of complexes can be provided based on (i) Precipitation of primary valencies on the addition of a suitable reagent.

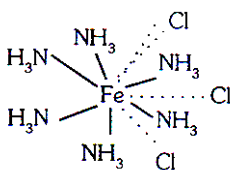
e.g. - $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$ forms 3 moles of AgCl in the form of precipitate on addition of AgNO_3 solution. This indicates that the complex ionises as



- (ii) Electrical conductance of complexes - More the number of ions provided greater is the electrical conductance of the complex in aqueous medium.

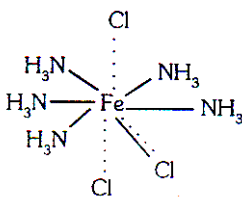
e.g. - The electrical conductance of aqueous $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$ is greater than that of aqueous solution of $[\text{Fe}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. $[\text{Fe}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \rightarrow [\text{Fe}(\text{NH}_3)_5\text{Cl}]^{+2} + 2\text{Cl}^-$ Total 3 ions

Representation of complexes – Werner's representation for $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$

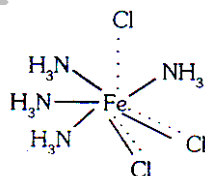


(Dotted lines indicate primary Valency and continuous lines indicate secondary valency of metal ion.) If the complex is

- (a) $\text{Fe}(\text{NH}_3)_5\text{Cl}_3$ Then in this complex 'Cl' groups act as primary valencies and one of the 'Cl' acts as secondary valency also. Thus werner's representation for this complex will be



- (b) $\text{Fe}(\text{NH}_3)_4\text{Cl}_3$ In this complex 'c' groups act as primary valencies and two of the 'c' group act as secondary valencies also. Thus this complex is represented as



- * **Modern representation of complexes** - Central metal ion along with secondary valencies or ligands are written in square brackets and primary valencies outside the square bracket.

For example :- $[\text{Fe}(\text{NH}_3)_6]\text{Cl}_3$

Coordination sphere or inner sphere - This is written in square bracket. This constitutes the central metal ion along with ligands.

Outer sphere or Ionisation sphere. This is written outside the square bracket. In aqueous solution the groups written outside the square bracket dissociate and are provided in the form of ions.

5 MODERN THEORY OF COMPLEXES OR ELECTRONIC THEORY OF COMPLEXES -

Sidgwick and Lowry in 1923 developed this theory, and modified Werner's Theory.

According to sidgwick the primary valency is regarded to be formed by transfer of electron and secondary valency is formed by the sharing of electron pair provided by the donar.

- * During formation of primary valency the metal loses electrons. Thus the number of electrons decrease during primary valency formation. In the formation of secondary valency the metal ion gains electrons in pairs for the formation of coordinate bond. Thus during secondary valency formation the total number of electrons associated with the metal ion increase.

- * The total number of electrons associated with the metal ion in its complex may be equal to or nearly equal to the atomic number of inert gas of the same period. This total number of electrons is called 'Effective atomic number' (E.A.N.) of the metal.

For e.g. - E.A.N. of cobalt in $(\text{Co}(\text{NH}_3)_6)^{3+}$ can be calculated as follows:

Atomic number of cobalt = 27

In this complex, cobalt is in +3 oxidation state, thus the number of electrons in Co^{+3} ion are
 $= 27 - 3 = 24$

During secondary valency formation Co^{+3} ion gains 6 pairs of electrons during coordinate covalent bonding.

Thus E.A.N. of cobalt in

$$\begin{aligned} [\text{Co}(\text{NH}_3)_6]^{+3} &= 24 + 12 \\ &= 36. \end{aligned}$$

i.e., E.A.N. = (No. of electron in the metal ion) + (No. of electrons gained from the ligands)

As the E.A.N. of cobalt is 36 in this complex, according to sidgwick, this complex will be stable. Though E.A.N. rule is applicable in many cases, there are several examples in which E.A.N. rule is not obeyed. For example $(\text{Cr}(\text{H}_2\text{O})_6)^{+3}$ EAN = 33

6. NOMENCLATURE OF COORDINATION COMPOUNDS -

The present system of nomenclature derived from the suggestions of **Alfred Werner** and recommended by the Inorganic Nomenclature Committee of the I.U.P.A.C. is given. The main rules of naming of complexes are

- (i) Like simple salts, the positive part of the coordination compound is named first. For e.g. $\text{K}_4[\text{Fe}(\text{CN})_6]$ the naming of this complex starts with potassium
- (ii) The ligands of the coordination sphere are to be named.
- (iii) The ligands can be neutral, anionic or cationic.
- (a) The neutral ligands are named as the molecule e.g. $\text{C}_5\text{H}_5\text{N}$ pyridine, $(\text{C}_6\text{H}_5)_3\text{P}$ Triphenyl phosphine, $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ethylene diamine.
 The neutral ligands which are not named as the molecule are
 CO carbonyl, NO nitrosyl, H_2O Aqua, NH_3 amine.
- (b) The negative ligands end in - 'O'.

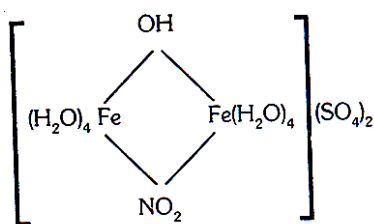
Cl^- chloro,	SO_4^{-2} sulphato	NO_2^- Nitro
ONO^- nitrito,	OH Hydroxo,	NH_2^- amido
NH^{-2} imido	NO_3^- nitrato,	CO_3^{-2} carbonato
CH_3COO^- acetato,	CN cyno	CNO cyanato etc.
- (c) Positive ligands naming ends in 'ium' $\text{NH}_2-\text{NH}_3^+$ Hydrazinium, NO_2^+ nitronium, NO^+ nitrosonium
- (iv) If ligands are present more than once, then their repetition is indicated by prefixes like di, tri, tetra etc.
- (v) When more than one type of ligand is present in the complex, then the ligands are named in the alphabetical order. (prior to this naming of ligands was followed in the order - negative, neutral and positive ligands)
- (vi) After naming of ligands the central metal ion is to be named followed by its oxidation state in Roman numbers in brackets. (as per IUPAC)
- (v) If the complex is neutral or provides a cationic complex ion, then the central metal ion is to be named as it is. If the complex provides anionic complex ion then the name of central metal ion ends in 'ate'
- (vii) After the naming of central metal ion anion which is in the outer sphere is to be named.

The naming of some of the complexes is done as follows :- (as per IUPAC)

(1) $\text{K}_4[\text{Fe}(\text{CN})_6]$

(anionic complex is present so suffix ate is added with metal's name) Potassium hexacyanoferrate (II)

- (2) $\text{K}_2[\text{PtCl}_6]$
Potassium hexachloroplatinate (IV)
- (3) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
(Cationic complex is present so metal is without any suffix) Hexamine cobalt (III) chloride
- (4) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_4]\text{Cl}$
Tetra aqua di chloro chromium (III) chloride
- (5) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$
Diamine tetra chloroplatinum (IV)
- (6) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (Neutral complex - hence no suffix is used with metal ion)
Triammine trichloro cobalt (III)
- (7) $\text{K}_3[\text{Co}(\text{NO}_2)_6]$
Potassium hexanitro cobaltate (III)
- (8) $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NO}]$
Sodium pentacyano nitrosyl ferrate (II)
- (9) $[\text{NiCl}_4]^{-2}$
Tetrachloro nickelate (II) ion
- (10) $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{+2}$
Pentammine chlororuthenium (III) ion
- (viii) When bidentate ligands are coordinated to the metal ion, their repetition is indicated by pre fixes like bis, tris, tetrakis etc. for example :
- (1) $[\text{Fe}(\text{en})_3]\text{Cl}_3$
Trisethylene diamine iron (III) chloride
- (2) $[\text{Ni}(\text{Gly})_2]$
Bis glycinato nickel (II)
- (ix) If a complex ion has two metal atoms then it is termed polynuclear. The ligand which connects the two metal ions is called as **Bridging Ligand or Bridge group**.
A prefix of Greek letter μ , is repeated before the name of each different kind of bridging group.



Octa aqua - μ , - hydroxo - μ - nitro diiron (III) sulphate.

7. ISOMERISM IN COMPLEXES -

Compounds which have the same molecular formula, but differ in their properties due to the difference in structure are called as Isomers. The phenomenon of exhibiting different structures is called as Isomerism. Isomerism is commonly considered, to be the characteristic of only organic compounds, it is also found although less frequently among inorganic substances.

7.1 Structural isomerism - It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere. The structural isomers are of following types

1. Ionisation isomers - The type of isomerism which is due to the exchange of groups or ion between the coordinating sphere and the ionisation sphere. This type of isomers yield different types of ions in solution,

For e.g.:

1. $\text{Co}(\text{NH}_3)_4 \text{Br}_2 \text{SO}_4$ can represent

$[\text{Co}(\text{NH}_3)_4 \text{Br}_2] \text{SO}_4$ (red violet) and $[\text{Co}(\text{NH}_3)_4 \text{SO}_2] \text{Br}$ (red). These complexes give sulphate ion and bromide ion respectively

2. $(\text{Pt}(\text{NH}_3)_4 \text{Cl}_2) \text{Br}_2$ and $[\text{Pt}(\text{NH}_3)_4 \text{Br}_2] \text{Cl}_2$

3. $[\text{Co}(\text{NH}_3)_4 (\text{NO}_3)_2] \text{SO}_4$ and $[\text{Co}(\text{NH}_3)_4 \text{SO}_4] (\text{NO}_3)_2$

2. **Hydrate isomers** - The water molecules may be associated with metal ions or they may appear in lattice positions without being closely associated with the metallic cation.

The complexes which differ with respect to the number of water molecules attached to the metal ion as ligands are called as Hydrate isomers.

For e.g. - $\text{Cr}(\text{H}_2\text{O})_6 \text{Cl}_3$ has three structures possible

(i) $[\text{Cr}(\text{H}_2\text{O})] \text{Cl}_3$ violet

(ii) $[\text{Cr}(\text{H}_2\text{O})_5 \text{Cl}] \text{Cl}_2 \text{H}_2\text{O}$ green

(iii) $[\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2] \text{Cl} \cdot 2\text{H}_2\text{O}$ dark green.

These complexes differ from one another with respect to the number of water molecules acting as ligands. They also differ in their number of primary valencies i.e., chloride ions which are provided. Other hydrate isomers are

$[\text{Co}(\text{NH}_3)_4 \text{H}_2\text{O Cl}] \text{Cl}_2$

$[\text{Co}(\text{NH}_3)_4 \text{Cl}_2] \text{Cl} \cdot \text{H}_2\text{O}$

3. **Linkage or salt isomers** - When a ligand has two different types of donor atoms but it is a monodentate ligand then this type of isomerism is exhibited. The ligand may get attached to the metal ion through either of the two donor atoms. For e.g. - NO_2^- ligand. In this ligand the coordinating sites are nitrogen (i.e., $-\text{NO}_2$ Nitro ligand) or through oxygen (i.e., ONO Nitrito ligand)

$[\text{Co}(\text{NH}_3)_5 \text{NO}_2]^{2+}$ and $[\text{Co}(\text{NH}_3)_5 \text{ONO}]^{2+}$ are linkage isomers of one another. .

The nitro isomer is yellow and is stable to acids whereas nitrito isomer is red and is decomposed by acids.

4. **Coordination isomers** - This type of isomerism is exhibited when the complex has two complex ions in it 'Cationic and anionic'. This type of isomerism is caused by the interchange of ligands and metal ions between the two complex ions of the same complex

e.g. - (i) $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]$

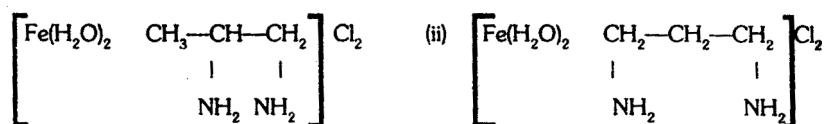
$[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{CN})_6]$

(ii) $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{C}_2\text{O}_4)_3]$

$[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{C}_2\text{O}_4)_3]$

5. **Ligand isomers** - Ligands with $\text{C}_3\text{H}_6(\text{NH}_2)_2$ have two different structures i.e., 1, 3-diamino propane and 1, 2-diaminopropane(propylene diamine). These complexes which have same molecular formula. but differ with respect to their ligands are called as Ligand isomers.

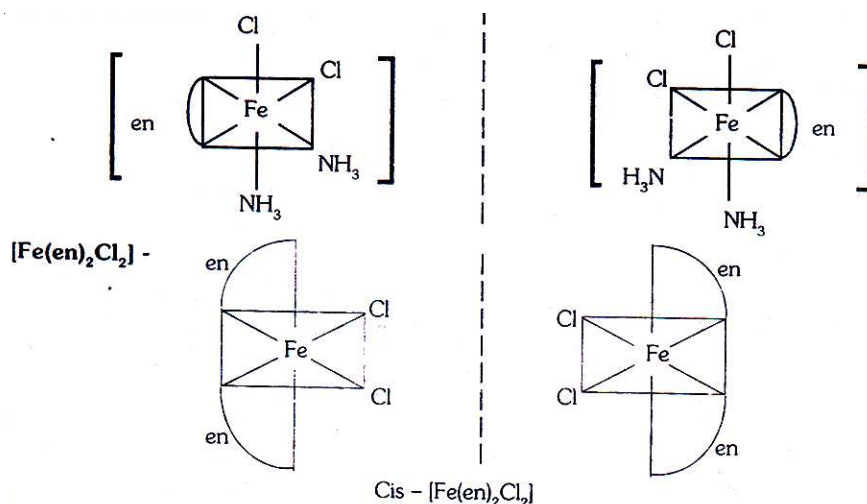
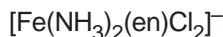
For e.g. - $[\text{Fe}(\text{H}_2\text{O})_2 \text{C}_3\text{H}_6(\text{NH}_2)_2 \text{Cl}_2]$ has two different structures



7.2 **Stereo isomers** - They have same molecular formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion. The two stereo isomers which are possible are - Geometrical and optical.

1. **Geometrical or cis-Trans isomer** - The ligands occupy different positions around the central metal ion. When two identical ligands are coordinated to the metal ion from same side then it is cis isomer. (in Latin, cis means same). If the two identical ligands are coordinated to the metal ion from opposite side then it is Trans isomer (in Latin, Trans means across). These geometrical isomers differ in physical as well as chemical properties.

- * Thus complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as optical isomers.
- * The 'd' and 'l' isomers of a compound are called as Enantiomers or Enantiomorphs. 4-coordinated complexes with tetrahedral geometry exhibit optical activity
- * Only those 6-coordinated complexes in which there are chelating agents i.e. bidentate ligands, exhibit optical isomerism For e.g.



- * Trans - $[\text{Fe}(\text{en})_2\text{Cl}_2]$ do not show optical activity due to superimposition of their mirror image.

8 BONDING THEORIES IN COMPLEXES

- * The main bonding theories of coordination compounds are

- I. Valence Bond Theory
- II. Crystal field Theory

9. VALENCE BOND THEORY -

This theory was mainly developed by **linus Pauling**. The main features of this theory are

- i. Every metal ion when it forms a complex compound undergoes formation of coordinate covalent bond. During this bond formation the metal ion acts as electron pair acceptor. For this the metal ion provides vacant orbitals. The number of vacant orbitals provided is equal to the coordination number of metal ion.
For e.g. -In the formation of $[\text{Fe}(\text{NH}_3)_6]^{3+}$, Fe^{+3} ion provides six vacant orbitals.
In $[\text{Cu}(\text{NH}_3)_4]^{2+}$, Cu^{+2} ion provides four vacant orbitals.
- ii. The metal provides vacant orbitals only after the process of hybridisation, thus vacant hybrid orbitals are provided by the metal ion.
- iii. The vacant hybrid orbitals of metal ion get overlapped by orbitals of ligands containing lone pair of electrons.- The number of such overlappings is equal to the coordination number of metal ion.
- iv. The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals. These complexes are called as Inner orbital complexes and outer orbital complexes respectively.
- v. If inner 'd' orbitals are involved in hybridisation, it is only through the pairing of unpaired electrons in the 'd' orbitals of metal ion. Then such type of complexes will be diamagnetic or less paramagnetic and will be called as Low spin complexes.

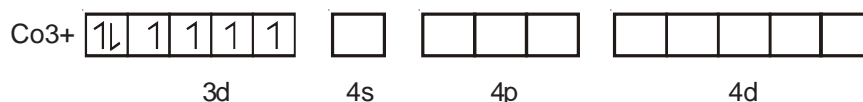
- * All outer orbital complexes have paramagnetic nature and they are called as High spin complexes.

- * Applications of valence Bond theory

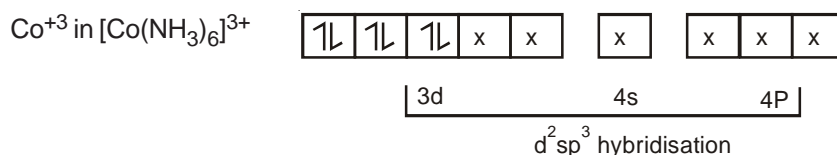
- I. To 6-coordinated complexes

- * $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic whereas $[\text{CoF}_6]^{-3}$ is paramagnetic.

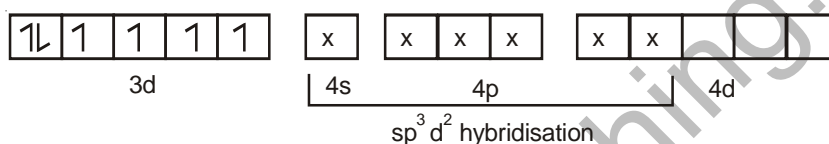
- * In the two complex ions Co^{3+} ion is present



As $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic the unpaired electrons get paired up due to strong ligand and the metal ion provides vacant '3d' orbitals for hybridisation.



- * It is an octahedral complex.
- * This is a diamagnetic complex. As inner 'd' orbitals are involved in hybridisation, it is an inner orbital complex and it is a low spin complex.
- As $[\text{CoF}_6]^{3-}$ is paramagnetic, the unpaired electrons remain as it is. Thus Co^{3+} in $[\text{CoF}_6]^{3-}$ will be



- * In this complex F^- is weak ligand therefore no pairing of e^- occurred.
- * It is an octahedral complex.
- This is a paramagnetic complex. The outer 'd' orbitals are involved in hybridisation, hence it is an outer orbital complex and a high spin complex.

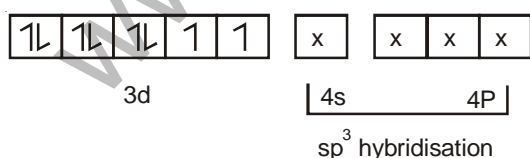
10. 4-COORDINATED COMPLEXES

- * $[\text{NiCl}_4]^{2-}$ is paramagnetic whereas $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic.
- Ni^{2+} ion has configuration of $[\text{Ar}] 3d^8$



The unpaired electrons remain as such, as it is a paramagnetic complex.

Thus Ni^{2+} in $[\text{NiCl}_4]^{2-}$ will be



- * In this complex Cl^- is weak ligand.
- * $[\text{NiCl}_4]^{2-}$ has tetrahedral geometry. It is an outer orbital complex and is a high spin complex.
- * $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic in nature. Thus the unpaired electrons in '3d' orbitals of Ni^{2+} get paired up.
- Ni^{2+} in $[\text{Ni}(\text{CN})_4]^{2-}$

12. FACTORS AFFECTING THE STABILITY OF COMPLEXES

The stability of complexes depends on the following factors

i. Nature of the central metal ion - Greater the charge density on the metal ion. greater the metal ion will have tendency to form the complex. Thus the complexes formed by metal ion with high charge density are more stable than complexes formed by metal ion with less charge density. For e.g. - Fe^{+3} ion forms a more stable complex than Fe^{+2} , Similarly Pt^{+4} complex is more stable than Pt^{+2} complex.

The stability of the complexes of some of the cations (having same charge but different ionic radii) decrease with the increase in ionic radii.

Ion	Cu^{+2}	Ni^{+2}	CO^{+2}	Fe^{+2}	Mn^{+2}
Ionic radii	0.69	0.78	0.82	0.83	0.91

ii. Nature of ligand

A strongly basic ligand forms a more stable complex with the metal ion that a ligand which is weakly basic in nature. Thus a cyano complex will be more stable than a chloro complex.

iii. When a bidentate ligand combines with the metal ion then a chelated complex is formed. This type of chelated complex will be more stable.

13. ORGANOMETALLIC COMPOUNDS OR C - METAL BOND COMPOUNDS

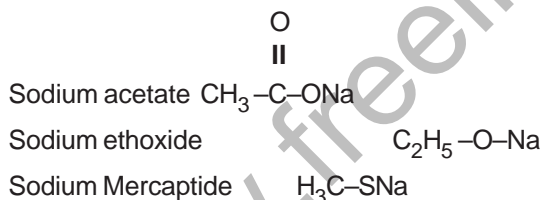
Introduction

Definitiaon - Compounds containing one or more metal carbon bonds.

* The compds of metalloids (Ge, Sb) and non metals (B, Si, P, As etc.) which are less electro -ve than carbon are also categorised in this title.

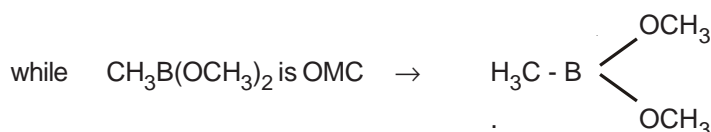
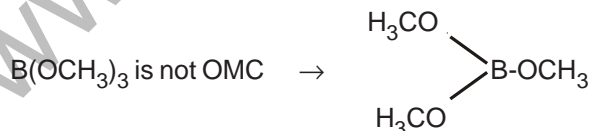
e.g $\text{R} - \text{Zn} - \text{R}$ dialkyl zinc (Frankland reagent)
 $\text{R} - \text{Mg} - \text{X}$ Alkyl Mg halide (Grignards reagent)

* **Compounds like**



are not organometallic compd. as

In these compounds metal is not directly attached with carbon atom.



* Cyanides, carbides and carbonates are not considered OMC because in these compds metal is not attached to carbon of alkyl gp. or carbon of carbonyl gp.

13.1 Classification of Organometallic Compounds

OMC can be classified into three main categories

(a) σ - bonded OMC :

These compounds are formed mostly by non transition and metalloid elements.

- eg. R - Mg - X, (grignard's reagent)
 $(\text{CH}_3)_2\text{Zn}$ (Dimethyl zinc or frankland's reagent)
 $(\text{R})_2\text{Cd}$, (dialkyl cadmium)
 $(\text{C}_2\text{H}_5)_4\text{Pb}$ (Tetra ethyl lead)
 $(\text{CH}_3)_3\text{Al}$, TiCl_4 (Ziegler natta catalyst) etc.

(b) π - bonded OMC :

These are usually formed by transition metals.

- eg. Ferrocene $[\text{Fe}(\eta^5 - \text{C}_5\text{H}_5)_2]$
 where η = No. of carbon atoms combined with metal atom.
 Zeise's salt $\text{K}[\text{PtCl}_3(\eta^2 - \text{C}_2\text{H}_4)]$
 Dibenzene chromium $[\text{Cr}(\eta^6 - \text{C}_6\text{H}_6)_2]$

(e) σ and π - bonded OMC :

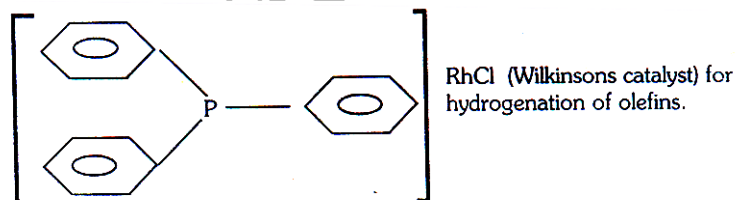
Transition metals of gp. 6, 7, 8, 9 and 10 in their zero oxidation state form such type of OMC.

The carbonyl compds. of these metals have both σ , and π bonds. e.g.

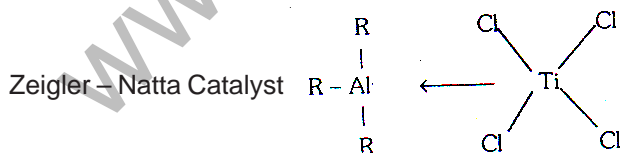
- $\text{INi}(\text{CO})_4$, $[\text{Fe}(\text{CO})_5]$, $[\text{Mn}_2(\text{CO})_{10}]$
 $[\text{M}(\text{CO})_6]$ where M is Cr, Mo, W.

13.2 Application 'of Organometallic Compounds

(1) As homogeneous Catalyst



(2) As heterogeneous catalyst



Tri alkyl Al ← Titanium tetrachloride used for - Polymerisation

- (3) **Organic synthesis** - OMC like R - Mg - X, $\text{R}_2 - \text{Cd}$, $\text{CH}_3 - \text{Li}$ etc. are used for preparation of almost all type of organic compds. .
- (4) **As petrol additive** - TEL (Tetraethyl lead) is used as antiknock compd. in petrol.
- (5) **In medicine** - Organo arsenic compds are used as medicine for syphilis deases.
- (6) **In agriculture** - Seeds are treated with ethyl Hg Chloride to protect the plants against infection.

f-Block Elements

They were earlier called as rare earth metals as it was believed that they exist in earth's crust to a very less extent for e.g. : Pm, does not exist in the earth's crust. But this terminology is now not applicable as they exist in earth's crust to a sufficient extent.

14. INNER TRANSITION ELEMENTS

The elements in which the additional electron enters in $(n - 2)f$ orbitals are called inner **transition elements**, or **f-block elements**.

14.1 Position in the periodic table

The lanthanides resemble yttrium in most of their properties. So it became necessary to accommodate all the fifteen elements together at one place. This has been done by placing the first element, lanthanum below yttrium and placing the remaining fourteen elements separately in the lower part of the periodic table.

Lanthanide series (Z = 58 - 71) (Ce – Lu)

Actinide series (Z = 90 - 103) (Th – Lw)

14.2 Lanthanides (Lanthanones)

Lanthanides are reactive elements so do not found in free state in nature. Most important minerals for lighter Lanthanides are - Monazite, cerites and orthite and for heavier lanthanides - Gadolinite and Xenotime

14.3 Electronic configuration

The general configuration of lanthanides may be given as $4f^{2-14}5s^25p^65d^{0/1}6s^2$. Lanthanide have outer three shells incomplete.

Atomic Number	Element	Symbol	Outer electronic configuration	
			Atomic	+3 ion
58	Cerium	Ce	$4f^2 6s^2$	$4f^1$
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^2$
60.	Neodymium	Nd	$4f^4 6s^2$	$4f^3$
61.	Promethium	Pm	$4f^5 6s^2$	$4f^4$
62.	Samarium	Sm	$4f^6 6s^2$	$4f^5$
63.	Europium	Eu	$4f^7 6s^2$	$4f^6$
64.	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7$
65.	Terbium	Tb	$4f^9 6s^2$	$4f^8$
66.	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^9$
67.	Holmium	Ho	$4f^{11} 6s^2$	$4f^{10}$
68.	Erbium	Er	$4f^{12} 6s^2$	$4f^{11}$
69.	Thulium	Tm	$4f^{13} 6s^2$	$4f^{12}$
70.	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{13}$
71.	Lutecium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14}$

It is to be noted here that filling of 4f orbitals in the atoms is not regular. A 5d electron appears in gadolinium (z = 64) with an outer electronic configuration of $4f^7 5d^1 6s^2$ (and not $4f^8 6s^2$). This is because the 4f and 5d electrons are at about the same potential energy and that the atoms have a tendency to retain stable half filled configuration.

On the other hand, the filling of f orbitals is regular in tripositive ions.

After losing outer electrons, the f orbitals shrink in size and became more stable. Pm is the only synthetic radioactive lanthanide.

Oxidation states

14.4	Lanthanides	Oxidation States
	Ce ₅₈	+3,+4
	Pr ₅₉	+3, (+4)
	Nd ₆₀	+3
	Pm ₆₁	+3
	Sm ₆₂	(+2), +3
	Eu ₆₃	+2,+3
	Gd ₆₄	+3
	Tb ₆₅	+3,+4
	Dy ₆₆	+3; (+4)
	Ho ₆₇	+3
	Er ₆₈	(+2), +3
	Tm ₆₉	(+2), +3
	Yb ₇₀	+2,+3
	Lu ₇₁	+3

* Oxidation states in brackets are unstable states

- * The lanthanides contains two s electrons in the outermost shell, they are therefore expected to exhibit a characteristic oxidation state of +2. But for the lanthanides, the +3 oxidation is common.
- * This corresponds to the use of two outermost electrons ($6s^2$) alongwith one inner electron. The inner electron used is a 5d electron (in La, Gd and Lu), or one of the 4f electron if no 5d electrons present.
- * All the lanthanides attains +3 oxidation state and only cerium, Praseodymium, and terbium exhibit higher oxidation state (+4).

Oxidation states + 2 and +4 occur particularly when they lead to

- (i) A noble gas configuration e.g. Ce⁴⁺ (f^0)
- (ii) A half filled 'f' orbital e.g. Eu²⁺, Tb⁴⁺, (f^7)
- (iii) A completely filled 'f' orbital e.g. Yb²⁺ (f^{14})

Therefore, in higher oxidation state, they act as oxidising while in lower state as reducing agents.

14.5 Magnetic properties

In tripositive lanthanide ions the number of unpaired electrons regularly increases from lanthanum to Gadolinium (0 to 7) and then continuously decreases upto lutecium (7 to 0). So lanthanum and lutecium ions which are diamagnetic, all other tripositive lanthanide ions are Paramagnetic.

Colour - The lanthanide ions have unpaired electrons in their 4f orbitals. Thus these ions absorbs visible region of light and undergo f-f transition and hence exhibit colour. The colour exhibited depends on the number of unpaired electrons in the 4f orbitals. The ions often with $4f^n$ configuration have similar colour to those ions having $4f^{14-n}$ configuration.

- * Lanthanide ions having $4f^0$, $4f^7$, $4f^{14}$ are colourless. Lanthanide ions $4f^1$ and $4d^{13}$ are also colourless.

14.6 Other Properties

(a) Highly dense metals with high m.pts. (do not show any regular trend).

(b) Ionisation Energies - Lanthanides have fairly low ionisation energies comparable to alkaline earth metals.

(c) Electro positive Character - High due to low I.P.

(d) Complex formation - Do not have much tendency to form complexes due to low charge density because of their large size.

Lu⁺³ is smallest in size can only form complex.

(e) Reducing Agent - They readily lose electrons so are good reducing agent.

- * In +3 oxidation states, nitrates, perchlorates and sulphates of lanthanides and actinides are water soluble, while their hydroxides, fluorides and carbonates are water insoluble.
- * Alloys of lanthanides with Fe are called misch metals.
- * $\text{La}(\text{OH})_3$ is most basic in nature while $\text{Lu}(\text{OH})_3$ least basic.
- * Lanthanides form MC_2 type carbide with carbon, which on hydrolysis gives C_2H_2 .

15. LANTHANIDE CONTRACTION

- * In the lanthanide series with increasing atomic number, there is a progressive decrease in the size from lanthanum to lutetium or from La^{+3} to Lu^{+3} . This contraction in size is known as lanthanide contraction.
- * The general electronic configuration of these elements is $4f^{0-14}5s^2p^6d^{0-1}6s^2$. In these elements the added electron enters the deep seated f-orbitals and therefore experiences considerable pull by the nucleus.
- * Such an electron cannot add to the size of the element and also because the intervening $5s^2p^6d^1$ electronic shells, it is very little screening effect on the outermost $6s^2$ electrons.
Hence with increasing atomic number, the enhanced nuclear charge leads to contraction in the size of atoms and ions.
- * The atomic volumes of europium and ytterbium are unexceptionally large. The large atomic size of Eu and Yb suggest weaker bonding in the solid elements. Both these elements have only two electrons extra than the stable configurations (half filled, f^7 , and completely filled, f^{14}), hence they utilise two electrons in metallic bonding as in the case with barium.

16. EFFECTS OF LANTHANIDE CONTRACTION

- (i) Close resemblance of Lanthanides** :- The general decrease in the sizes of the lanthanides with an increase in their nuclear charges result in a small increase in their ionisation energies. Hence their basic and ionic nature gradually decreases from La to Lu.

This also explains the variations in properties such as increased tendency for hydrolysis and formation of complex salts and decreased thermal stability. solubility of their salts.

- (ii) Similarity of yttrium with lanthanides** :- The properties of yttrium are so similar to the lanthanides that it is considered more a member of the lanthanide series than a congener of scandium.

- (iii) Anomalous behaviour of post-lanthanides** :- The following anomalies may be observed in the behaviour of post-lanthanide elements.

(a) Atomic size - The ionic radii of Zr^{+4} is about 9% more than Ti^{+4} . Similar trend is not maintained on passing from the second to third transition series. The ionic radius of Hf^{+4} , instead of increasing (because of inclusion of one more electronic shell), decreases (or is virtually equal to Zr^{+4}) as a consequence of the lanthanide contraction.

This explains the close similarities between the members of the second and third transition series than between the elements of the first and second series.

(b) Ionisation potential and electronegativity :- The effect of lanthanide contraction is also seen in the increase in the ionisation potential values and electronegativities of the elements of the third transition series, contrary to the general trend.

Because of the lanthanide contraction, the post-lanthanide elements have stronger positive field and thus the electrons are held more tightly.

The greater effective nuclear charge of the former make them more electronegative than the latter.

(c) High density :- Because of lanthanide contraction the atomic sizes of the post lanthanide elements become very small. consequently, the packing of atoms in their metallic crystals become so much compact that their densities are very high.

The densities of the third transition series elements are almost double to those of the second series elements.

17. APPLICATION OF LANTHANIDES

Cerium is most useful element in the lanthanides

- (a) Ceramic application - CeO_2 , La_2O_3 , Nd_2O_3 and Pr_2P_3 are used as decolourizing agents for glasses.
- (b) CeS (m.p. - 2000°C) is used in the manufacture of a special type of crucibles and refractories.
- (c) Lanthanide compounds like cerium molybdate, cerium tungstate are used as paints and dyes.
- (d) In textile and leather industries (Ce salts).

18. ACTINIDES (5f - BLOCK ELEMENTS)

- * The elements in which the extra electron enters 5f-orbitals of (n - 2)th main shell are known as actinides.
- * The man-made eleven elements Np_{93} - Lr_{103} are placed beyond uranium in the periodic table and are collectively called trans-uranic elements.
- * Th, Pa and U first three actinides are natural elements.

18.1 Electronic configuration :-

The general configuration of actinides may be given as $5f^{1-14} 6d^{0/1}, 7s^2$.

Atomic No.	Elements	Symbol	Electronic Configuration
90	Thorium	Th	$6d^2 7s^2$
91	Protactinium	Pa	$5f^2 6d^1 7s^2$
92	Uranium	U	$5f^3 6d^1 7s^2$
93	Neptunium	Np	$5f^4 6d^1 7s^2$
94	Plutonium	Pu	$5f^6 7s^2$
95	Americium	Am	$5f^7 7s^2$
96	Curium	Cm	$5f^7 6d^1 7s^2$
97	Berkellium	Bk	$5f^9 7s^2$
98	Californium	Cf	$5f^{10} 7s^2$
99	Einsteinium	Es	$5f^{11} 7s^2$
100	Fermium	Fm	$5f^{12} 7s^2$
101	Mandeleevium	Md	$5f^{13} 7s^2$
102	Nobelium	No	$5f^{14} 7s^2$
103	Lawrencium	Lw	$5f^{14} 6d^1 7s^2$

18.2 Oxidation states

In lanthanides and actinides +3 oxidation is the most common for both of the series of elements. This oxidation state becomes increasingly more stable as the atomic number increases in the actinide series.

Actinides	Oxidation state*
Th_{90}	+4
Pa_{91}	(+4), +5
U_{92}	(+3), (+4), (+5), +6
Np_{93}	(+3), (+4), +5, (+6), (+7)
Pu_{94}	(+3), +4, (+5), (+6), (+7)
Am_{95}	+2, (+3), (+4), (+5), (+6)
Cm_{96}	+3, (+4)
Bk_{97}	+3, (+4)
Cf_{98}	+3
Es_{99}	+3
Fm_{100}	+3
Md_{101}	+3
No_{102}	+3
Lw_{103}	+3