

Section-I: d-Block elements

8.1 INTRODUCTION

The elements in which last electron enters into $(n - 1)d$ orbital are known as d-block elements. These are also known as transition metals because they show intermediate properties between s-block and p-block elements. d-block elements are,

- Transition elements** : These elements contain incompletely filled $(n - 1)d$ orbital in their elementary state or in any of their common oxidation state.
- Typical transition metals** : These elements have incompletely filled $(n - 1)d$ orbital and they show variable oxidation state, ability to form complex compound and to form colored compounds.
- Non typical transition metals** : They have completely filled $(n - 1)d$ orbitals, i.e. $(n - 1)d^{10}$ configuration in elementary state as well as in the form of ion.

e.g. Zn, Cd, Hg, Uub are excluded from transition series. But these are considered as transition elements because their chemical behavior is similar to the transition elements.

8.2 ELEMENTS IN d-SERIES

There are four series of d-block elements in the periodic table. They are called 3d, 4d, 5d, and 6d series depending upon filling of 3d, 4d, 5d and 6d orbital of $(n - 1)$ th main shell.

All these series contain 10 elements each.

8.3 POSITION IN PERIODIC TABLE

- These elements are placed in the middle part between s-block and p-block elements in the periodic table.
- The d-block elements belong to group 3 to 12 and 4 to 7 period (series).

8.4 ELECTRONIC CONFIGURATION

Series	Elements	General elec. conf.
3d series	$_{21}\text{Sc} - _{30}\text{Zn}$	$[\text{Ar}], 3d^{1-10}, 4s^{1-2}$
4d series	$_{39}\text{Y} - _{48}\text{Cd}$	$[\text{Kr}], 4d^{1-10}, 5s^{1-2}$
5d series	$_{71}\text{La}$ and $_{72}\text{Hf} - _{80}\text{Hg}$	$[\text{Xe}], 4f^{1-14}, 5d^{1-10}, 6s^{1-2}$
6d series	$_{89}\text{Ac}$ and $_{104}\text{Rf} - _{112}\text{Uub}$	$[\text{Rn}], 5f^{1-14}, 6d^{1-10}, 7s^2$

Electronic configuration of 3d-Series

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

8.5 OCCURRENCE

- Soft elements of d-block occur as sulphide minerals.
- More electropositive and hard d-block elements occur as oxide minerals.
- Oxide minerals are reduced with carbon to get metals.
- Sulphide minerals are roasted in air to get metals.
- Titanium**: It occurs in combined state. It is found in small quantity in coal, clay, rocks, sand etc.
- Vanadium**: It occurs as vanadate of lead, zinc, copper etc. in the ore of vanadinite and carnotite.
- Chromium**: It occurs in the ore, Chromite: $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, Chrome ochre: Cr_2O_3 , Crocoisite: PbCrO_4 .
- Manganese**: It does not occur in free state. It occurs in ore like pyrolusite MnO_2 and other minerals.
- Iron**: The abundance of iron is next to aluminium.

in earth crust. It occurs free as well as combined states.

10. Cobalt: It is present in nickel and arsenic ore and also present in soil.
11. Nickel: It is present in cobalt ore.
12. Copper: It is found in rock, soil, sea, mineral water and important ore are,
 Cuprite: Cu_2O
 Malachite: $[\text{CuCO}_3, \text{Cu(OH)}_2]$
 Azurite: $[2\text{CuCO}_3, \text{Cu(OH)}_2]$ etc.
13. Zinc : It is found in nature in association with silver, Cu, lead, Pt in their ores.

8.6 GENERAL TRENDS IN PROPERTIES OF FIRST ROW TRANSITION SERIES OR 3d-SERIES

The members belonging to a given transition series do not differ from one another in same period. It is due to fact that in transition series no change in the numbers of electrons in outer most shell and only change occurs in the $(n-1)d$ electrons from one member to another member in period.

Atomic and Ionic radii :

1. Atomic size or radii: From Sc to Zn atomic size decreases with increase in atomic number but this decrease become very small.
 - i) From Sc to Cr atomic number increases and also nuclear charge increase which result pull ns electron inward i.e. it tends to reduce size. At the same time addition of extra electron in $(n-1)d$ orbitals also provides shielding effect. As the number of d-electron increases shielding effect increases. Hence from Sc to Cr atomic size decreases.
 - ii) From Cr to Cu effective nuclear charge and shielding effect become nearly equal and hence there is no change in atomic radii from Cr to Cu.
 - iii) The value of atomic size at end of the each series is higher. This is due to electron-electron repulsions among $(n-1)d$ electron. These repulsion is higher in zinc, hence zinc has more size than Cu metal.

Ionic radii: Ionic radii also follows similar trend as observed in atomic radii.

From above table it is observed that ionic radii decreases with increasing oxidation

state. This is due to increase in effective nuclear charge.

2. **Metallic character:** All the transition elements are metals and shows all the properties which are characteristic of metals. They are hard, possess metallic luster, high density, high M.P., high B.P., malleability, ductility, conductors of heat and electricity etc. Nearly all transition metal have hexagonal closed packed (HCP), cubic closed packed (CCP), body centre cubic (BCC) structures which are the characteristic of true metals.

The metallic character of transition elements depends upon their low ionization energy and unpaired electrons in ns-orbitals and d-orbitals. Cr, Mo, W are very hard metals as they have more number of unpaired d-electrons while Zn, Cd and Hg are softer in nature as they don't have any unpaired d-electrons.

3. **Melting and boiling point:** The transition metals have very high M.P. and B.P. It decreases with increase in atomic number.
 - i) The high M.P. and B.P. of transition elements depends upon force of attraction which binds their atoms together i.e. in their crystal lattice.
 - ii) The presence of one or more unpaired d-electrons results the formation of covalent bonding and therefore to high M.P. [However this concept do not explain why manganese (Mn) and technetium (Tc) having five unpaired electrons in d-orbitals possess lower M.P. than vanadium or cobalt which have only three unpaired d-electrons. The complex structure is responsible for this abnormal behavior.]
 - iii) In particular transition series the number of unpaired electron in $(n-1)d$ sub shell increases up to middle i.e. up to d^5 configuration. Therefore the strength of metallic bonding increases and hence the M.P. and B.P. increases up to d^5 configuration.
 - iv) Beyond d^5 configuration the electron start pairing up and the number of unpaired electron decreases on moving further in series. This decrease in the strength of metallic bonds and hence M.P. and B.P. decreases after the middle of series. e.g. In 3d series, as

atomic number and unpaired electron increases up to chromium. (Sc-d¹, Ti-d², V-d³, Cr-d⁵). Therefore strength of metallic bonding increases and the M.P. and B.P. also increases from Sc to Cr. Chromium has maximum M.P. in 3d series.

After chromium number of unpaired electron in 3d-orbitals decreases (Fe-d⁴, Co-d³, Ni-d²). Therefore strength of metallic bonding decreases and the M.P. and B.P. also decreases from Cr to Cu.

- v) Zn, Cd, Hg have no unpaired electrons i.e. d¹⁰ configuration. These metals are soft and have low M.P. and B.P.
- vi) Hg is liquid at room temperature and has M.P. 234K.
- vii) Manganese (Mn), technetium (Tc) and Re have abnormally low M.P.

4. **Density:** The densities of transition metals are high. The high density of transition metal is due to large number unpaired electrons in (n-1)-d orbitals due to which they have strong metallic bonding and possess high densities. Osmium has highest density 22.6 g/ml, where as scandium (Sc) has lowest density 2.99 g/ml and it is lightest transition element.

5. **Atomization:** Combination of atom is known as atomization and energy release during combination is known as atomization energy. Atomization of element depends upon number of unpaired electrons in d-orbitals. More the unpaired electron more the atomization and more the atomization energy. The maximum value of atomization lies at middle of series because of more number of unpaired electron in d-orbitals.

6. **Ionization energy (IE) of 3d transition series or 4d row transition series:**

- i) The ionization energy of d-block element lies in between s-block and p-block elements. The ionization energy of d-block element is more than s-block element and less than p-block elements.
- ii) From Sc to Zn ionization energy increases as atomic size decreases but not a regular trend.
- iii) In case of Sc, Ti, V and Cr the value IE are close to each other, similarly IE value of Fe,

Co, Ni and Cu are almost similar.

- iv) As we move from Sc to Cu the nuclear charge or effective nuclear charge increases by one unit because at each element single electron enters into (n-1)d orbitals.
- v) The shielding effect of d-orbitals is poor. The effect of increases nuclear charge is more than that of shielding effect of d-orbitals. Hence atomic size decreases from Sc to Cu. Therefore IE increases, quite slowly among the d-block elements.
- vi) The IE value of zinc is higher due to stability of completely filled 3d orbitals. Second and Third ionization energy also increase in a series. However, some exceptions are observed.
- vii) The 1st ionization energy of 5d series element (third transition series) is higher than 3d and 4d transition series.

Explanation: The atom of element in 5d series possesses filled 4f-orbitals which has poor shielding effect due to its diffused shape, as a result the effect of increase nuclear charge is more than shielding effect of 4f-orbitals, hence atomic size decreases. Therefore 1st IE of 5d series is more than that of 3d and 4d-series elements.

7. **Ionization energy and thermodynamic stability of transition metal compounds:** Ionization energy value of transition metal is used to know the thermodynamic stability of compounds. Smaller the sum of ionization energy of metal to attain a particular oxidation state, greater is the stability of the compound of that metal in that particular oxidation state.

For example:

- i) Ni²⁺ compounds are more stable than Pt²⁺ compounds
- ii) Pt⁴⁺ compounds are more stable than Ni⁴⁺ compounds.

Explanation: The first four IE of Ni and Pt are

IE value	IE ₁ + IE ₂	IE ₃ + IE ₄	IE ₁ + IE ₂ + IE ₃ + IE ₄
Element	KJ/mole		
Ni	2.49×10^3	8.8×10^3	11.29×10^3
Pt	2.66×10^3	6.7×10^3	9.36×10^3

- i) From above data it is clear that first and second ionization energy of nickel is less than platinum.

This indicates that the ionization of Ni to Ni^{2+} ion requires less energy than the energy required by Pt to Pt^{2+} . Therefore Ni^{2+} compounds are thermodynamically more stable than Pt^{2+} compounds.

- ii) The sum of four IE energy of platinum is less than nickel. This indicates that the ionization of Pt to Pt^{4+} requires less energy than the energy required for the ionization of Ni to Ni^{4+} . Thus Pt^{4+} compounds are more stable than Ni^{4+} compounds. For example: K_2PtCl_6 is a well known compound in which Pt is tetravalent while corresponding nickel compound i.e. K_2NiCl_4 is not known.

8. Oxidation State:

- a) The energy difference between ns and (n-1)d orbitals are almost same, therefore electrons from

these levels are available for bonding. Hence transition metal shows variable oxidation state.

- b) The variable oxidation state of transition metals are related to electronic configuration.

e.g. i) Scandium: It has electronic configuration $3d^1, 4s^2$. Hence shows +2 and +3 oxidation.

But +3 oxidation state is more stable. It forms compound mainly in +3 oxidation state

- ii) Titanium: It has outer electronic configuration $3d^2, 4s^2$. Hence shows +2, +3, +4 oxidation state. But +4 oxidation state is more stable.

- iii) Vanadium: It has outer electronic configuration $3d^3, 4s^2$. Hence shows +2 to +5 oxidation state. But +5 oxidation state is more stable.

Oxidation State

Element	M	M^{1+}	M^{2+}	M^{3+}	M^{4+}	M^{5+}	M^{6+}	M^{7+}
21^{Sc}	$3d^1, 4s^2$	-	$3d^1, 4s^0$	$3d^0, 4s^0$				
22^{Ti}	$3d^2, 4s^2$	-	$3d^2, 4s^0$	$3d^1, 4s^0$	$3d^0, 4s^0$			
23^{V}	$3d^3, 4s^2$	-	$3d^3, 4s^0$	$3d^2, 4s^0$	$3d^1, 4s^0$	$3d^0, 4s^0$		
24^{Cr}	$3d^5, 4s^1$	$3d^5, 4s^0$	$3d^4, 4s^0$	$3d^3, 4s^0$	$3d^2, 4s^0$	$3d^1, 4s^0$	$3d^0, 4s^0$	
25^{Mn}	$3d^5, 4s^2$	-	$3d^5, 4s^0$	$3d^4, 4s^0$	$3d^3, 4s^0$	$3d^2, 4s^0$	$3d^1, 4s^0$	$3d^0, 4s^0$
26^{Fe}	$3d^6, 4s^2$	-	$3d^6, 4s^0$	$3d^5, 4s^0$	$3d^4, 4s^0$	$3d^3, 4s^0$	$3d^2, 4s^0$	
27^{Co}	$3d^7, 4s^2$	-	$3d^7, 4s^0$	$3d^6, 4s^0$	$3d^5, 4s^0$	$3d^4, 4s^0$		
28^{Ni}	$3d^8, 4s^2$	-	$3d^8, 4s^0$	$3d^7, 4s^0$	$3d^6, 4s^0$			
29^{Cu}	$3d^{10}, 4s^1$	$3d^{10}, 4s^0$	$3d^9, 4s^0$					
30^{Zn}	$3d^{10}, 4s^2$	-	$3d^{10}, 4s^0$					

Sc = +2, +3

Ti = +2, +3, +4

V = +2, +3, +4, +5

Cr = +1, +2, +3, +4, +5, +6

Mn = +2, +3, +4, +5, +6, +7

Fe = +2, +3, +4, +5, +6

Co = +2, +3, +4, +5

Ni = +2, +3, +4

Cu = +1, +2 Zn = +2

According to Hund's rule elements in d^0, d^5, d^{10} configuration gives stable oxidation state.

For example: Stability of some oxidation state

$\text{Ti}^{4+}(3d^0, 4s^0) > \text{Ti}^{3+}(3d^1, 4s^0)$

$\text{Fe}^{3+}(3d^5, 4s^0) > \text{Fe}^{2+}(3d^6, 4s^0)$

$\text{Mn}^{2+}(3d^5, 4s^0) > \text{Mn}^{3+}(3d^4, 4s^0)$

- c) The most common oxidation state of transition

element is +2.

- d) Element in higher oxidation i.e. +4 and above are good oxidizing agent

e.g. i) $\text{K}_2\text{CrO}_4, \text{K}_2\text{Cr}_2\text{O}_7, \text{CrO}_2\text{Cl}_2$ are good oxidizing agent.

ii) Iron in +2 oxidation state is known as ferrous while in +3 oxidation state are ferric. Fe^{3+} is powerful oxidizing agent than Fe^{2+}

- e) Mostly ionic compounds are formed in +2, +3 oxidation state while covalent compounds are formed in higher oxidation state by sharing of d-electrons.

e.g. CuCl_2 is ionic while $\text{MnO}_4^-, \text{CrO}_4^{2-}, \text{O}_3, \text{O}_4$ are covalent.

- f) Higher oxidation state is stabilized by high electronegative element like O or F, while lower oxidation state (zero or +1) is stabilized by ligand

like carbonyl (CO), which can accept electron from the metal through π -bonding. The highest oxidation state by transition element is +8 which is for Os and Ru e.g. Ru^{+8} , Os^{+8}

9. Reducing property:

- Atoms or ions having tendency to lose electrons are reducing agents.
- The reducing property of these metals depends upon atomic size, ionization energy.
- Lower the I.P. of metal stronger is the reducing property. From left to right in transition metal atomic radius decreases and IE increases and thus reducing property decreases. But at the end of period atomic radius slightly increases due to more electron-electron repulsion and thus reducing property increases.
- Down the group atomic radius increases up to second transition series, but in 3rd and 4th transition series atomic radius almost same due to lanthanide contraction. Therefore reducing property increases from 1st to 2nd and then decreases.

10. Catalytic properties:

- The property of a metal to acts as catalyst to increase rate of a chemical reaction is known as catalytic property. Transition metal and their compounds are known for their catalytic properties. The commonly used catalyst are Fe, Pt, Pd, Ni, Co, Cr, Mn and V_2O_5 etc.
- This catalytic activity is the formation of unstable intermediate complexes and to adopt multiple oxidation state. In some cases, transition metals provide unpaired d-electrons to form the unstable intermediate compound with the reactants. These intermediate compounds readily decompose to give final product and original catalyst.



Substrate Catalyst Intermediates product Catalyst

- In some cases, the transition metal cation can change their oxidation state to become most effective catalyst e.g. Fe^{3+} catalyses the reaction between iodide and persulphate ion as,



Net reaction: $2\text{I}^- + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{I}_2 + 2\text{SO}_4^{2-}$

iv) **Table** : Some important examples of catalytic property of transition metals

Transition metal/comp.	Used as catalyst in
1. Pt	Manufacture of H_2SO_4 Manufacture of NH_3 by Haber's process. Hydrogenation of oils into fats. Oxidation of SO_2 into SO_3 in contact process of manufacturing of H_2SO_4
2. Fe and Mo	
3. Ni	
4. V_2O_5	
5. MnO_2	The decomposition of KClO_3 to obtain O_2
6. $\text{TiCl}_4/\text{TiCl}_3$	
7. Co-Th alloys	It is used in Ziegler Natta catalyst for preparation of high density polyethylene. Fischer Tropsch process in the synthesizing gasoline.
8. Fe^{3+} catalyst	
9. Cu	It catalyse reaction between iodide and persulphate ion as, $2\text{I}^- + \text{S}_2\text{O}_8^{2-} \longrightarrow \text{I}_2 + 2\text{SO}_4^{2-}$ Manufacture of $(\text{CH}_3)_2\text{SiCl}_2$ used to make silicones.
10. CuCl_2	
	Manufacture of Cl_2 from HCl .

11. Formation of interstitial compounds:

Compounds which are formed by d-block and f-block metals by trapping small atoms like H, C, N, B inside the vacant space in their crystal lattice.

Transition metal have defect in their crystal lattice and shows variable oxidation state hence they form number of interstitial compounds.

These compounds are non-stoichiometric in nature as don't have definite composition and neither typical ionic nor covalent. e.g. TiC , $\text{TiH}_{1.73}$, Mn_4N , Fe_3H , $\text{VH}_{0.56}$, $\text{ZrH}_{1.92}$ etc.

As the vacant space in the crystal lattice of metal is filled up by C, H, N, B hence interstitial compounds have new properties.

- Their chemical properties are same as that of parent metal
- They are very hard and show more electrical and thermal conductivity than parent metal.
- They have high melting point than parent metal because metal-nonmetal bond is stronger than metal-metal pure bond.
- Their densities are less than parent metals.
- Hydrides of transition metals are powerfully reducing agents.
- The metallic carbides are chemically inert and very hard like diamond.

Note:

Steel and cast iron are the example of interstitial compounds of iron and carbon. In these compounds, the malleability and ductility of iron is lost, whereas the tenacity of metal increases.

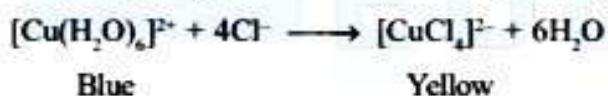
12. **Alloy formation:** Transition metals forms a large number of alloys. The tendency to form alloys in transition metal is due to quite similar in atomic size, the atom of one metal can be substitute by atom of another metal in its crystal lattice. Thus on cooling a mixture solution of two or more transition metals, smooth solid alloys are formed. e.g. Brass (Cu-Zn), Bronze (Cu-Sn), Steel and stainless steel (It is alloys of iron with Cr, V, Mo, W, Mn).

Alnico which is an alloy of Al (12%), Ni (20%), Co (50%) and rest of Fe is used to make permanent magnets.

13. **Colors:** In general color of the transition ion can be related to

- Presence of unpaired d-electrons
- d-d transition
- Ligands attached to metal ion
- Geometry of complex.

Color also depends upon ligands and geometry of complex e.g. When CuSO_4 dissolve in water it form blue solution of complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ which was octahedral geometry. But when the solution is treated with cone. HCl it turn yellow. This change is due to formation of another complex $[\text{CuCl}_4]^{2-}$ which has tetrahedral geometry.



- e) Charge transfer.

Color of $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , MnO_4^- , Cu_2O and Ni-DMG complex are due to charge transfer transition.

14. **Magnetic properties:**

- Ions which contain unpaired electrons are paramagnetic and don't contain unpaired electrons are diamagnetic.
- The number of unpaired electrons increases the paramagnetic character also increases. Maximum paramagnetic character is also known as ferromagnetism.
- The paramagnetic substances have effective magnetic moment μ_{eff} which is

given by the expression. This relation is called "spin only".

Formula to determine magnetic properties is

$$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B.M}$$

Where n = number of unpaired electrons.

B.M. = Bohr magneton

$$1 \text{ B.M.} = \frac{eh}{4\pi mc}$$

Where, h = Plank's constant, e = Charge on electron c = Velocity of light, m = Mass of electron

8.7 PREPARATION AND PROPERTIES OF $\text{K}_2\text{Cr}_2\text{O}_7$ AND KMnO_4

A] Preparation and properties of $\text{K}_2\text{Cr}_2\text{O}_7$

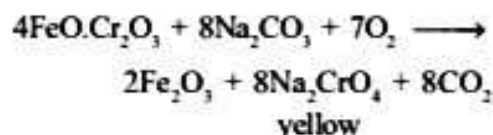
- 8.7.1: **Manufacture of $\text{K}_2\text{Cr}_2\text{O}_7$ from chromite ore**
The formula of ore is $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, it is also called as chrome iron ore.

Manufacture of $\text{K}_2\text{Cr}_2\text{O}_7$ from chromite ore involves four steps.

Step-1: Purification of chromite ore :

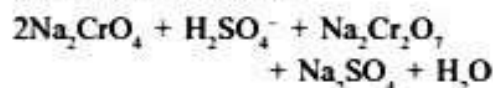
Powdered chromite ore is washed with water by hydrolic classifier. Lighter gangue is carried away by water while heavier chromite ore settles at bottom.

- Step-2: Roasting of chromite ore to produce sodium chromate:** Purified ore is mixed with Na_2CO_3 (soda-ash) and lime stone (CaCO_3) and roasted with excess of air in furnace to produce yellow coloured sodium chromate. Lime stone is added to keep the mass porous for easier oxidation.



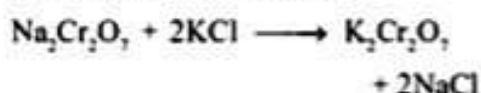
Roasted mass is washed with water, sodium chromate goes in solution and insoluble substances are separated by filtration.

Step-3: Conversion of sodium chromate in sodium dichromate:



Step-4: Conversion of sodium dichromate

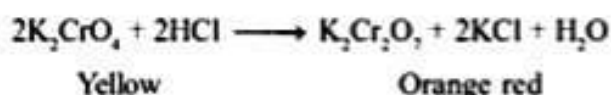
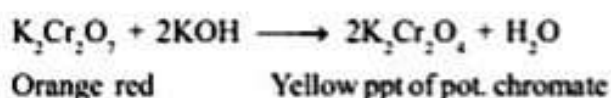
in potassium dichromate:



The solution is concentrated and hot solution is cooled. The less soluble $\text{K}_2\text{Cr}_2\text{O}_7$ crystallize out first leaving behind NaCl in solution. The orange red coloured crystals of $\text{K}_2\text{Cr}_2\text{O}_7$ is filtered and purified by recrystallization.

8.7.2: CHEMICAL PROPERTIES OF $\text{K}_2\text{Cr}_2\text{O}_7$

1. Action of alkali :



In alkaline medium chromate ion (CrO_4^{2-}) is present, while in acidic medium dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) is present. Both ions are equilibrium at $\text{pH} = 7$

2. **Oxidising properties:** Potassium dichromate act as good oxidising agent in acidic medium by gain of six electrons. In this process chromium change its oxidation state +6 to +3. The equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic medium is 49. It can

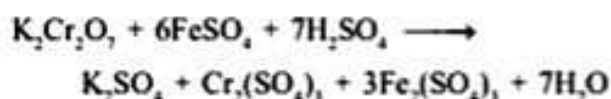
$$\text{be calculated as } \frac{\text{Mol. Wt}}{6} = \frac{294}{6} = 49$$



O.S of Cr = +6 O.S of Cr = +3

e.g. i) Reaction with ferrous sulphate:

It oxidises ferrous sulphate to ferric sulphate. In this reaction $\text{K}_2\text{Cr}_2\text{O}_7$ reduced to chromic sulphate. Orange red color of $\text{K}_2\text{Cr}_2\text{O}_7$ turn green.

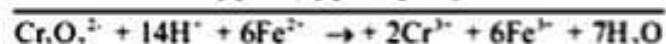
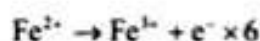


Reaction can be represented using ionic equation.

Reduction:

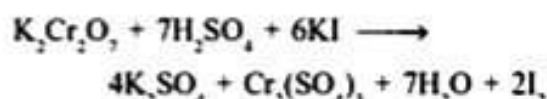


Oxidation:

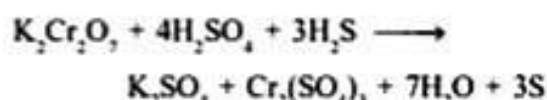


ii) **Reaction with KI :** Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ oxidises KI to iodine and itself reduced into chromic sulphate.

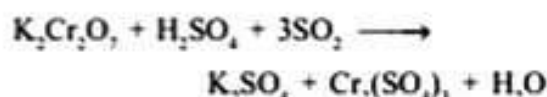
Liberated iodine turn solution brown.



iii) **Reaction with H_2S :** Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ oxidises H_2S into sulphur and itself reduced into chromic sulphate. Orange red color of solution turn green.



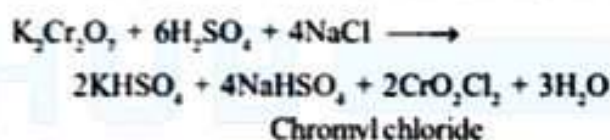
iv) **Reaction with SO_2 :** Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ oxidises SO_2 into K_2SO_4 and itself reduced into chromic sulphate. Orange red color changes to green. This reaction is used to test for SO_2 gas.



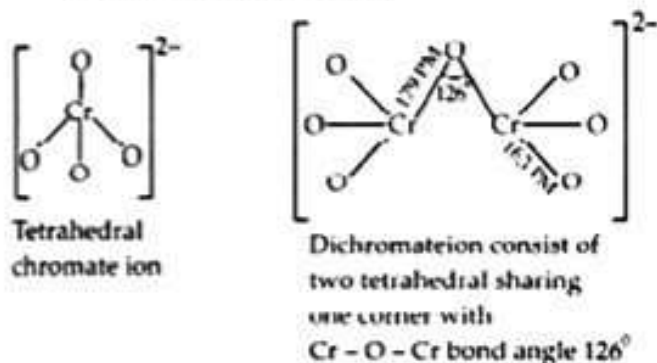
v) **Oxidation of 1° alcohols, secondary alcohols, aldehyde and ketones:**

Refer alcohol unit – 11

3. **Chromyl chloride test or Test of chloride ion or reaction with NaCl/KCl :** When mixture of metal chloride, potassium dichromate and H_2SO_4 is heated gives red fumes of chromyl chloride. This test is used to detect chloride ion.



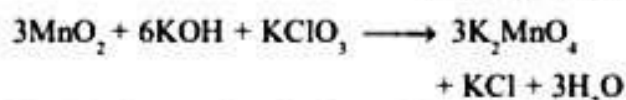
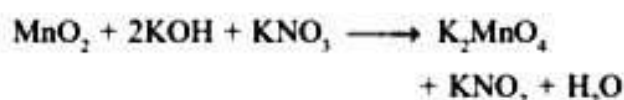
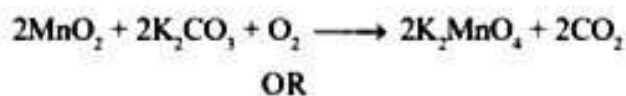
8.7.3 Structure of chromate ion (CrO_4^{2-}) and dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$)



B] Preparation and properties of KMnO_4

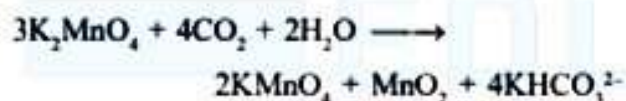
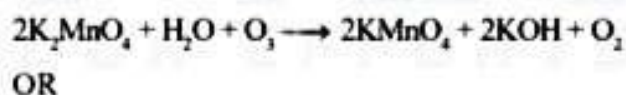
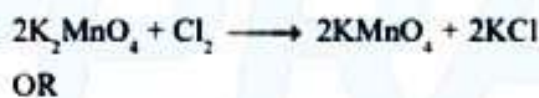
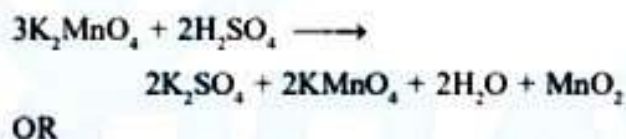
8.7.4: Preparation of KMnO_4 from MnO_2 (Pyrolusite ore or Hausmannite)

Manganese oxide is fused with KOH or K_2CO_3 in the presence of air or oxidising agent like KNO_3 or $KClO_3$, a green color K_2MnO_4 (potassium manganate) is obtained

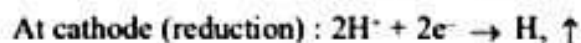
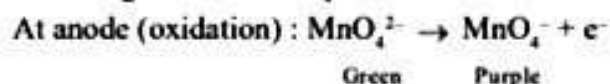


The fused mass obtained containing K_2MnO_4 is treated with water and then converted into $KMnO_4$ either oxidation or by electrolysis.

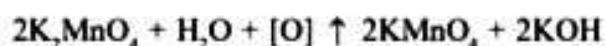
- a) **By oxidation:** Potassium manganate is treated with H_2SO_4 or CO_2 or Cl_2 or O_3 , the disproportionation reaction takes place to give potassium permanganate.



- b) **By electrolysis:** This is most preferred method. The potassium manganate solution is electrolyzed between iron cathode and nickel anode. The following reaction takes place.



The oxygen evolved at anode convert potassium manganate to potassium permanganate



8.7.5 PHYSICAL PROPERTIES

- It is deep purple crystalline solid.
- It is slightly soluble in water at room temperature

(6.4g / 100 g of water at room temperature).

8.7.6 CHEMICAL PROPERTIES

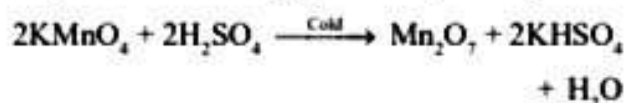
1. Action of heat:



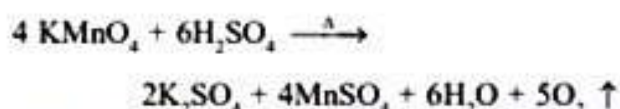
At red heat K_2MnO_4 further decompose to give potassium manganite and oxygen.



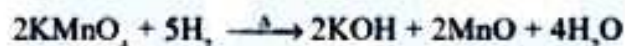
2. **Action of cold conc. H_2SO_4 :** Potassium permanganate is reacted with conc. H_2SO_4 in cold condition gives manganese heptaoxide (explosive oil) which on heating gives MnO_2 and O_2



3. **Action of hot conc. H_2SO_4 :** Potassium permanganate is heated with conc. H_2SO_4 gives $MnSO_4$, K_2SO_4 and O_2 gas.



4. **Action of H_2 :** Solid potassium permanganate is heated in current of H_2 gas gives KOH, MnO and water vapors.



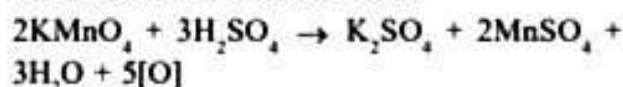
5. **Oxidising property of $KMnO_4$:** Potassium permanganate acts as oxidising agent in acidic, alkaline and neutral medium.

- a) **Oxidising agent in acidic medium:** It act as oxidising agent in acidic medium by gain of five electrons.

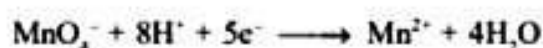
In this reaction oxidation state of Mn changes from +7 to +2. Thus equivalent weight of $KMnO_4$ in acidic medium is one fifth of its molecular mass

$$\text{i.e. } \frac{158}{5} = 31.6$$

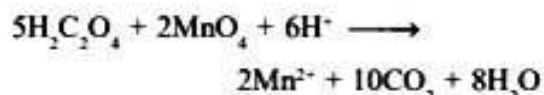
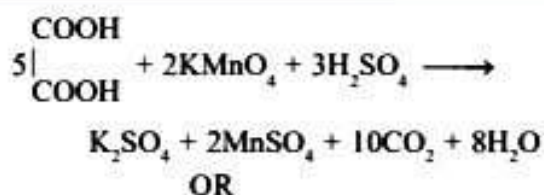
In acidic medium manganous sulphate is formed. The solution become colourless.



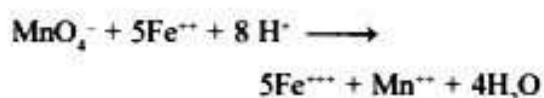
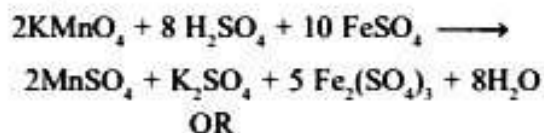
OR



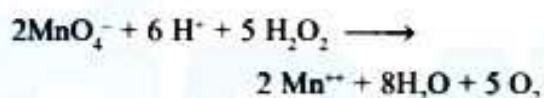
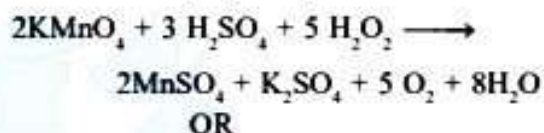
- e.g. i) **It oxidises oxalic acid to CO_2 :**



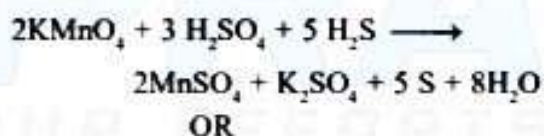
ii) **It oxidises ferrous sulphate to ferric sulphate:**



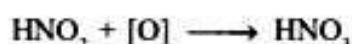
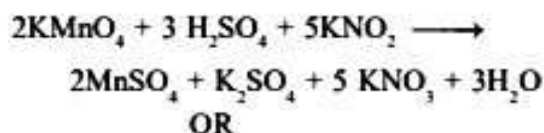
iii) **It oxidises H_2O_2 to O_2 :**



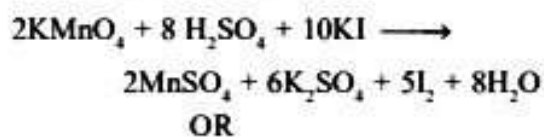
iv) **It oxidises H_2S to sulphur:**



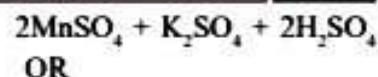
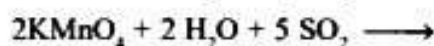
v) **It oxidises potassium nitrite to potassium nitrate:**



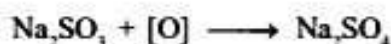
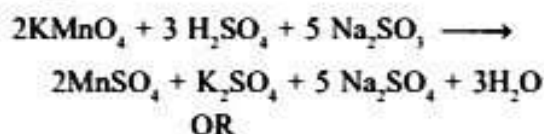
vi) **It oxidises KI to iodine:**



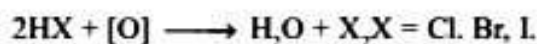
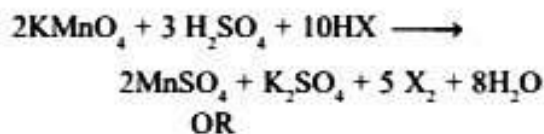
vii) **It oxidises SO_2 to H_2SO_4 :**



viii) **It oxidises sodium sulphite to sodium sulphate:**

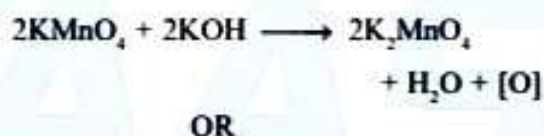


ix) **It oxidises HCl, HBr, HI to halogens**



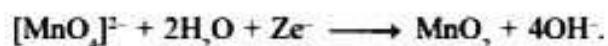
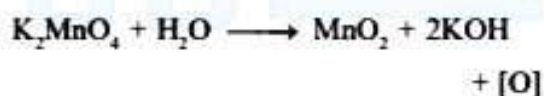
b) **Oxidizing agent in alkaline medium:**

i) KMnO_4 is reduced by KOH to give potassium manganate. Color changes first from purple to green and finally solution become brown.



O.S. of Mn = +7 O.S. of Mn = +6

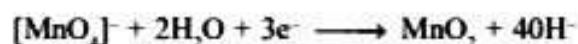
ii) In the presence of reducing agent potassium manganate reduced to brown colour MnO_2 .



S. of Mn = +6

O.S. of Mn = +4

The overall equation to show KMnO_4 as oxidising agent in alkaline medium is,



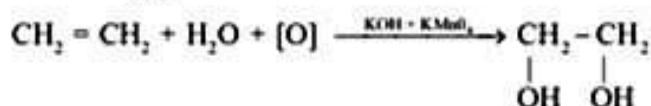
Potassium permanganate act as oxidising agent in alkaline medium by gain of three electrons. In this reaction oxidation state of Mn changes from +7 to +6 or +7 to +4.

Thus equivalent weight of KMnO_4 in alkaline medium is one third of it's molecular

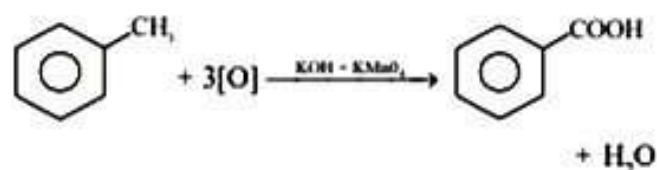
mass,

$$\text{i.e. } \frac{158}{3} = 52.6$$

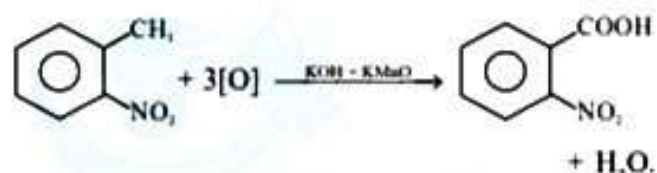
- e.g. i) Alkaline KMnO_4 is known as Baeyer's reagent, it oxidises ethylene to ethylene glycol



- ii) Alkaline KMnO_4 oxidises toluene to benzoic acid



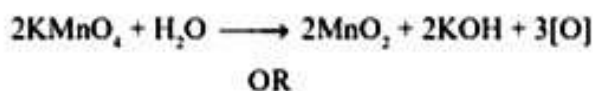
- iii) Alkaline KMnO_4 oxidises nitrotoluene to nitro benzoic acid



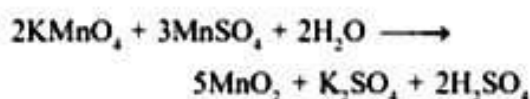
- c) **Oxidising agent in neutral medium :** In neutral medium MnO_2 is formed and solution become brown. In neutral medium KMnO_4 gain three electrons and act as oxidising agent. In this reaction oxidation state of Mn changes from +7 to +4.

Thus equivalent weight of KMnO_4 in neutral medium is one third of its molecular mass, i.e.

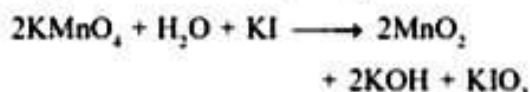
$$\frac{158}{3} = 52.6$$



- e.g. i) KMnO_4 in neutral medium oxidises manganous sulphate to manganese dioxide



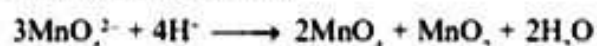
- ii) KMnO_4 in neutral medium oxidises KI to potassium iodate (KIO_3)



8.8 DISPROPORTIONATION OF OXIDATION STATE OF MANGANESE (Mn)

Manganese shows different oxidation states i.e. +2, +3, +4, +5, +6 and +7. When lower oxidation state is unstable as compared to higher oxidation state or vice versa then it undergoes disproportionation.

e.g. Manganese in +6 oxidation is unstable as compare to higher oxidation +7 and +4 oxidation state in acidic solution.



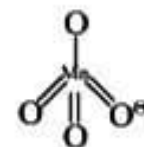
O.S. of Mn = +6 Mn = +7 Mn = +4

8.9 STRUCTURE OF MANGANATE ION AND PERMANGANATE ION

1. **Manganate ion (MnO_4^{2-}) :** It has tetrahedral geometry. Manganate ion is green in colour and paramagnetic because of presence of one unpaired electron.



2. **Permanganate (MnO_4^-) :** It has tetrahedral geometry. Permanganate ion is purple in colour and diamagnetic. Manganese in MnO_4^- under goes sp^3 hybridisation and hence four oxygen atoms arranged tetrahedrally, π bond is formed by overlapping of d-orbital of manganese and p-orbital of oxygen. Hence Mn^{7+} has d^0 configuration. So the deep purple colour arises from charge transfer and not d-d transition.



8. 10 Uses of KMnO_4

It is used

1. as disinfectants.
2. as oxidising agent in industry and laboratory.
3. Baeyer's reagent for detection of unsaturation.
4. In volumetric estimation of ferrous salt, oxalic acid, H_2O_2 etc.
5. For detecting halides in qualitative analysis.

Section-II : f-Block elements

(Rare earth elements or inner transition elements)

Definition:

The elements in which last electron enters into anti penultimate or prepenultimate shell or $(n-2)$ orbitals are known as f-block elements. These elements show intermediate properties of electropositive and electronegative elements.

General electronic configuration:

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

Where $n = 6$ for lanthanides, $n = 7$ for actinides

f-block elements are divided into two series:

1. **4f-series (Lanthanides)** : 14 elements.

2. **5f-series (Actinides)** : 14 elements.

In all 28 elements from atomic number 58 to 71 and from 90 to 103 are called f-block elements.

LANTHANIDES

(Lanthanoid or rare earth elements or 4f series or 1st inner transition series)

Introduction:

1. Symbol used for this series is Ln.
2. Name of this series is due to lanthanum, because properties of all these elements (14) similar to lanthanum. The lanthanum is prototype of lanthanoids.
3. This series starts from 55Ce to 71Lu

Definition:

The elements in which last electrons enters into 4f orbitals are known as lanthanides.

Position in periodic table:

1. These are placed in III B group and 6th row in the periodic table.
2. Actual position in between La and Hf (hafnium).

Occurrence :

1. These are rarely found in earth crust. Hence these are named as rare earth elements.
2. Each lanthanide mineral contains all elements except Promethium, because it is radioactive and short lived.

Lanthanide mineral divided in to two sub groups -

- a) **Cerium subgroup:** It contain elements of atomic number 57 to 62.
- b) **Ytterbium subgroup:** It contain elements of atomic number 63 to 71.

- c) Well known alloy of lanthanide is misch metal (La, Fe and traces of S, C, Ca, Al) which is used to make bullet and shells.

Electronic configuration:

1. It is observed that 4f and 5d-orbitals have nearly same energy. Hence two electronic configuration are suggested i.e. expected (idealised or probable) and observed (spectroscopic or accepted or actual)

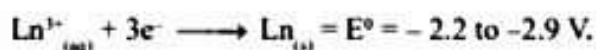
Elements	Symbol	Outer electronic config. [Xe]	and at. no.	expected	observed
Lanthanum	$_{57}\text{La}$	$6s^2, 4f^0, 5d^1$			$6s^2, 4f^1, 5d^0$
Cerium	$_{58}\text{Ce}$	$6s^2, 4f^1, 5d^1$			$6s^2, 4f^2, 5d^0$
Prasodymium	$_{59}\text{Pr}$	$6s^2, 4f^2, 5d^1$			$6s^2, 4f^3, 5d^0$
Neodymium	$_{60}\text{Nd}$	$6s^2, 4f^3, 5d^1$			$6s^2, 4f^4, 5d^0$
Promethium	$_{61}\text{Pm}$	$6s^2, 4f^4, 5d^1$			$6s^2, 4f^5, 5d^0$
Samarium	$_{62}\text{Sm}$	$6s^2, 4f^5, 5d^1$			$6s^2, 4f^6, 5d^0$
Europium	$_{63}\text{Eu}$	$6s^2, 4f^6, 5d^1$			$6s^2, 4f^7, 5d^0$
Gadolinium	$_{64}\text{Gd}$	$6s^2, 4f^7, 5d^1$			$6s^2, 4f^7, 5d^1$
Terbium	$_{65}\text{Tb}$	$6s^2, 4f^8, 5d^1$			$6s^2, 4f^9, 5d^0$
Dysprosium	$_{66}\text{Dy}$	$6s^2, 4f^9, 5d^1$			$6s^2, 4f^{10}, 5d^0$
Holmium	$_{67}\text{Ho}$	$6s^2, 4f^{10}, 5d^1$			$6s^2, 4f^{11}, 5d^0$
Erbium	$_{68}\text{Er}$	$6s^2, 4f^{11}, 5d^1$			$6s^2, 4f^{12}, 5d^0$
Thulium	$_{69}\text{Tm}$	$6s^2, 4f^{12}, 5d^1$			$6s^2, 4f^{13}, 5d^0$
Ytterbium	$_{70}\text{Yb}$	$6s^2, 4f^{13}, 5d^1$			$6s^2, 4f^{14}, 5d^0$
Lutetium	$_{71}\text{Lu}$	$6s^2, 4f^{14}, 5d^1$			$6s^2, 4f^{14}, 5d^1$

The complete general electronic configuration of lanthanides can be represented as

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

Chemical properties

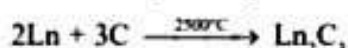
Earlier members of lanthanides are quite reactive, similar to calcium. But atomic number increases they behave more like aluminium.



1. **Reaction with hydrogen** : They combine with hydrogen produces hydride.



2. **Reaction of carbon:** Lanthanides are heated with carbon at 2500°C gives carbide having formula Ln_3C , Ln_2C_3 and Ln_2C ,

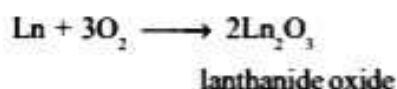


lanthanide carbide

3. **Reaction with H_2O :** Lanthanides are heated with H_2O gives basic lanthanide hydroxide.



4. **Reaction with oxygen :** They burn in air produces oxides and carbonates.



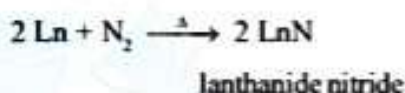
- a) Lanthanide oxide react with water to form insoluble hydroxide.



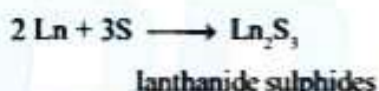
- b) Lanthanide oxide react with CO_2 in air gives carbonates.



5. **Reaction with nitrogen:** Lanthanides are heated with nitrogen gives nitride.



6. **Reaction with sulphur :** Lanthanides are heated with sulphur give sulphides.



7. **Reaction with mineral acid :** Lanthanides are treated with mineral acids liberated hydrogen gas as they have reduction potential ($E^\circ = -2$ to -2.4 V).



Lanthanide contraction :

Discovery : In 1925 Van Hevesy and Y.M. Goldschmidt has work on lanthanide contraction.

Definition: "The steady decrease in atomic and ionic size of lanthanide elements with increasing atomic number is known as lanthanide contraction."

Cause of lanthanide contraction:

- As we move from Ce to Lu, nuclear charge or effective nuclear charge increases by one unit at each elements because addition of 14-electrons in 4f-orbitals.
- The shielding effect of 4f-electrons is very less or poor, which is due to diffused shape of 4f-orbital.
- Hence 4f-electrons are not able to shield

perfectly the attraction between nucleus and outermost electronic orbit.

- The effect of increased nuclear charge is more than that of shielding effect of 4f-orbitals. Hence atomic or ionic size decreases from Ce to Lu.

The following points may be noted:

- Lanthanide contraction is related to atomic or ionic size.
- From Ce to Lu the atomic size decreases from 183 to 173 Pm and decrease only 10 Pm (0.1 Å).
- From Ce to Lu the ionic size decreases from 103 to 85 and decrease only 18 Pm (0.18 Å).
- The lanthanide contraction is due to imperfect shielding of 4f-electrons in the same orbitals.
- Due to similar size or lanthanide contraction, their separation in pure state is difficult.

Effect of lanthanide contraction or consequence of lanthanide contraction:

- Basicity of Ln and Ln^{3+} ions - (Reducing property):
 - Basicity or reducing property of atoms or ions depends upon tendency to lose electrons.
 - Greater the tendency to lose electron, stronger reducing agent or more basic will be the atoms or ion.
 - From Ce to Lu atomic or ionic size decreases. Hence tendency to lose electron decreases, basicity of ion decreases.
 - Decreasing order of basicity of Ln^{3+} ion is -
 $La^{3+} > Ce^{3+} > Pr^{3+} > > Lu^{3+}$.
- Basicity of hydroxide:**
 - Lanthanide forms basic hydroxide of the type $Ln(OH)_3$.
 - Basicity of hydroxide depends upon degree of dissociation, which is depends upon bond length between M-O and ionic character of $M(OH)_3$.
 - From La to Lu atomic size, bond length between M-OH decreases and hence ionic character decreases and covalent character increases.
 - That is why basicity of $M(OH)_3$ decreases from $La(OH)_3$ to $Lu(OH)_3$.
 - Decreasing order of ionic character and basicity of $Ln(OH)_3$ is,
 $La(OH)_3 > Ce(OH)_3 > Pr(OH)_3 > Nd(OH)_3 > > Lu(OH)_3$.
 - Increasing order of covalent character of $Ln(OH)_3$ is,

$\text{La(OH)}_3 < \text{Ce(OH)}_3 < \text{Pr(OH)}_3 < \text{Nd(OH)}_3 < \dots < \text{Lu(OH)}_3$

3. Atomic size of post lanthanide:

- Generally from top to bottom, atomic size increases.
- But due to lanthanide contraction, elements present in 2nd and 3rd transition series (d-block elements) have same size.
- Due to same size of Hf(hafnium) –

Zr(zirconium), Ta(tantalum) Nb(niobium), W(wolfram) Mo(molybdenum), Re(rhenium)– Tc(technetium), Os(osmium)–Ru(ruthenium). These pair of elements occurs together in nature, and hence they have same properties. These pair of elements are known as chemical twins. Chemical twins are – Hf – Zr, Ta – Nb, W – Mo, Re – Tc, Os – Ru.

Group →	4 th	5 th	6 th	7 th	8 th
1st transition series	Titanium Ti (132)	Vanadium V (122)	Chromium Cr (118)	Manganese Mn (117)	Iron Fe (117)
2nd transition series	Zirconium Zr (145)	Niobium Nb (134)	Molybdenum Mo (130)	Technetium Tc (127)	Ruthenium Ru (125)
3rd transition series	Hafnium Hf (144)	Tantalum Ta (134)	Tungsten W (130)	Rhenium Re (128)	Osmium Os (126)

Oxidation state

- Lanthanide shows +2, +3, +4, oxidation state by loss of two, three, four electrons respectively.
 - +3 oxidation state is principal and common oxidation state of all lanthanides.
 - +2 and +4 oxidation state are unstable and revert in to +3 oxidation state by loss and gain of electrons respectively.
- i) **+2 Oxidation state:** It is possible of loss of $2e^-$ from 6s-orbitals.



- a) +2 oxidation state is possible in Nd, Sm, Eu, Tm, Yb.

Decreasing order of reducing property is,



Reducing property of Eu^{2+} is less due to stable 4f⁷ configuration

- b) The elements in +2 oxidation state exist in solution and act as reducing agent (oxidised easily).

ii) +3 Oxidation state:

- a) It is possible by loss of $3e^-$ (two from 6s and one from 5d or 4f-orbitals).



- It is possible in all lanthanides.
- Elements in +3 oxidation state exist in solution and solid state, and acts as reducing agents (oxidised easily).
- The reducing property decreases from

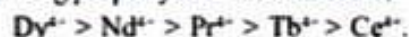


iii) +4 Oxidation state:

- a) It is possible by loss of $4e^-$ (two from 6s, one from 4f and one from 5d or two from 4f orbitals).



- It is possible in Ce, Pr, Nd, Tb, Dy.
- Elements in +4 oxidation state exists in solution and act as oxidising agents (reduced easily).
- Oxidising property decreases in order,



SUMMARY TABLE OF OXIDATION STATE OF ELEMENTS

Ele.	Oxidation state	M	Outer electronic configuration [Xe]		
			M ²⁺	M ³⁺	M ⁴⁺
⁵⁷ La	+3	6s ² , 4f ⁰ , 5d ¹	---	6s ⁰ , 4f ⁰ , 5d ⁰	---
⁵⁸ Ce	+3, (+4)	6s ² , 4f ² , 5d ⁰	---	6s ⁰ , 4f ¹ , 5d ⁰	6s ⁰ , 4f ⁰ , 5d ⁰
⁵⁹ Pr	+3, (+4)	6s ² , 4f ³ , 5d ⁰	---	6s ⁰ , 4f ² , 5d ⁰	6s ⁰ , 4f ¹ , 5d ⁰
⁶⁰ Nd	(+2), +3, +4	6s ² , 4f ⁴ , 5d ⁰	6s ⁰ , 4f ⁴ , 5d ⁰	6s ⁰ , 4f ³ , 5d ⁰	6s ⁰ , 4f ² , 5d ⁰
⁶¹ Pm	+3	6s ² , 4f ⁵ , 5d ⁰	---	6s ⁰ , 4f ⁴ , 5d ⁰	---
⁶² Sm	(+2), +3	6s ² , 4f ⁶ , 5d ⁰	6s ⁰ , 4f ⁶ , 5d ⁰	6s ⁰ , 4f ⁵ , 5d ⁰	---
⁶³ Eu	+2, +3	6s ² , 4f ⁷ , 5d ⁰	6s ⁰ , 4f ⁷ , 5d ⁰	6s ⁰ , 4f ⁶ , 5d ⁰	---
⁶⁴ Gd	+3	6s ² , 4f ⁷ , 5d ¹	---	6s ⁰ , 4f ⁷ , 5d ⁰	---
⁶⁵ Tb	+3, (+4)	6s ² , 4f ⁹ , 5d ⁰	---	6s ⁰ , 4f ⁸ , 5d ⁰	6s ⁰ , 4f ⁷ , 5d ⁰
⁶⁶ Dy	+3, (+4)	6s ² , 4f ¹⁰ , 5d ⁰	---	6s ⁰ , 4f ⁹ , 5d ⁰	6s ⁰ , 4f ⁸ , 5d ⁰
⁶⁷ Ho	+3	6s ² , 4f ¹¹ , 5d ⁰	---	6s ⁰ , 4f ¹⁰ , 5d ⁰	---
⁶⁸ Er	+3	6s ² , 4f ¹² , 5d ⁰	---	6s ⁰ , 4f ¹¹ , 5d ⁰	---
⁶⁹ Tm	(+2), +3	6s ² , 4f ¹³ , 5d ⁰	6s ⁰ , 4f ¹³ , 5d ⁰	6s ⁰ , 4f ¹² , 5d ⁰	---
⁷⁰ Yb	(+2), +3	6s ² , 4f ¹⁴ , 5d ⁰	6s ⁰ , 4f ¹⁴ , 5d ⁰	6s ⁰ , 4f ¹³ , 5d ⁰	---
⁷¹ Lu	+3	6s ² , 4f ¹⁴ , 5d ¹	---	6s ⁰ , 4f ¹⁴ , 5d ⁰	---

It may be noted that, the 4f-orbitals in lanthanides are deeply buried inside the atom. Hence, following properties can be occurred :

- They are not able to show variable oxidation state as compare to actinides.
- Chemistry of lanthanide is quite similar.
- They do not form complex compounds involving 4f-orbitals.
- They do not form covalent compounds but form ionic compounds like Ln(OH)₃.

Formation of complexes:

- Complex forming tendency depends upon small atomic size or ionic size, high nuclear charge, tendency to accept electron and availability of electrons.
- The lanthanides ion have high charge but their size being large and 4f-orbitals are deeply buried inside the atom, do not take part in bonding, hence they do not form complex.

Magnetic property :

- Ion which contain unpaired electron are paramagnetic which those contain paired electron are diamagnetic.
- Among the lanthanide La³⁺, Lu³⁺, Yb²⁺ which

have 4f⁰ and 4f¹⁴ configuration are diamagnetic while other trivalent lanthanide are paramagnetic.

iii) Paramagnetism is maximum in Ce.

Paramagnetism of lanthanides is easy to explain by simple formula $\mu_{eff} = \sqrt{n(n+2)}$.

Where n = number of unpaired electrons. More the value of n the more the paramagnetism.

ACTINIDES

(5f-series or actinons or second inner transition series or actinoids)

Introduction: Symbol used for this series is An.

Name of the series is due to actinium because properties of all these elements similar to that of actinium. The actinium is prototype of actinides. This series start from thorium to lawrencium.

Definition:

The elements in which last electrons enters into 5f-orbitals are known as actinides.

Position in periodic table :

The position of actinides in the periodic table is suggested by Seaborg in 1944.

Similarities between lanthanides and actinides :

1. In both the series, three outermost shells are partly filled while remaining inner shells are completely filled. The two electrons are present in outermost energy shell (ns^2). The penultimate energy shell ($n - 1$) $s^2p^6d^{0-1}$ contains 8 to 9 electrons. The anti penultimate energy shell ($n - 2$) $s^2p^6d^{10}f^{0-14}$ contains 19 to 32 electrons.
2. The elements of the both series shows common +3 oxidation state.
3. The elements of both series are electropositive

metal. They are reactive metals and acts as a strong reducing agents (oxidised easily).

4. The elements of both series shows contraction effect. Contraction effect is due to poor (imperfect) shielding of 4f orbitals for lanthanide and 5f-orbitals for actinides.
5. Cations with unpaired electrons in both the series are paramagnetic.

Formation of complexes of actinides:

Complex forming tendency of actinides is more than that of lanthanides.

