

—: D & F Block:—

D block:— also called transition element. is defined as the one which has incompletely filled d-orbitals in its ground state or in any of its oxidation state.

Atomic No	Element	Electronic Configuration
21	Scandium (Sc)	[Ar] 3d ¹ 4s ²
22	Titanium (Ti)	[Ar] 3d ² 4s ²
23	Vanadium (V)	[Ar] 3d ³ 4s ²
24	Chromium (Cr)	[Ar] 3d ⁵ 4s ¹
25	Manganese (Mn)	[Ar] 3d ⁵ 4s ²
26	Iron (Fe)	[Ar] 3d ⁶ 4s ²
27	Cobalt (Co)	[Ar] 3d ⁷ 4s ²
28	Nickel (Ni)	[Ar] 3d ⁸ 4s ²
29	Copper (Cu)	[Ar] 3d ¹⁰ 4s ¹
30	Zinc (Zn)	[Ar] 3d ¹⁰ 4s ²

Electronic Configuration:— (n-1) d¹⁻¹⁰ ns¹⁻²
 stands for inner orbitals which may have 1 to 10 electrons. may have 1 or 2 electrons.

- 1st Transition Series:— 3d → (Scandium) Sc(21) ←→ (Zinc) Zn(30)
- 2nd Transition Series:— 4d → (Yttrium) Y(39) ←→ (Cadmium) Cd(48)
- 3rd Transition Series:— 5d → [Lanthanum] La(57) [Lanthanoids] [Holmium] (HP) ←→ (Mercury) Hg(80)
- 4th Transition Series:— 6d → [Actinium] Ac(89) [Actinoids] [Rutherfordium] Rf(104) ←→ end.

Properties of Transition Elements:—

1) **Physical properties:**— The transition elements display typical metallic properties, high tensile strength, ductility, malleability, high thermal & electrical conductivity.

- The transition metals (with the exception of Zn, Cd & Hg) are very much hard & have low volatility.
- They have high melting & boiling points i.e., they have high enthalpy of atomisation.
- Along transition series the melting & boiling point 1st inc↑ as no. of unpaired electron per d-orbital inc↑ & after that start dec↓ as electron start getting paired up.

Ques:— Zn, Cd & Hg are soft & have low melting & boiling point why?

Ans:— It is becoz, they have fully filled (n-1)d orbitals & hence; the interatomic metallic bonding is not that strong.

2) **Atomic Radii & Ionic Radii:**— In general, transition elements along a given series show a progressive ↓ in radius due to ↑ in effective nuclear charge.

- But the ↓ with in the series is quite small becoz ↑ in nuclear charge is partially cancelled by shielding effect provided by the electrons being added.

in the inner d-orbital.

- Along the transition series the ↓ in metallic / atomic radius coupled with ↑ in atomic mass results in ↑ in density ($\rho = \frac{m}{V}$).

3) Ionisation Enthalpy:— Due to ↑ in nuclear charge, there is an ↑ in I.E along a transition series from left to right.

- The relative difference in I.E of any 2 consecutive d-block element is smaller than those of s & p-block elements.
- I.E also tell us about relative stabilities of various oxidation states.

	$I.E_1 + I.E_2$	$I.E_1 + I.E_2 + I.E_3 + I.E_4$ ($J \text{ mol}^{-1}$)
Ni	2.49×10^3	11.29×10^3
Pt	2.66×10^3	9.36×10^3

Stability:— Ni (II) > Pt (II); as sum of $I.E_1$ & $I.E_2$ is lesser for Ni (require less energy) (require more energy)

Pt (IV) > Ni (IV); as $I.E_1 + I.E_2 + I.E_3 + I.E_4$ is lower for Pt.

Qus 1:— $K_2[PtCl_6]$ exists while corresponding Ni compound is unknown why?

Ans:— It is becoz O.S of Ni is not very stable as the sum of first four I.E for Ni is high.

Qus 2:— I.E of Zn, Cd & Hg are very high why?

Ans:— It is becoz of fully filled stable electronic configuration i.e. $(n-1)d^{10}ns^2$.

Qus 3:— The 2nd I.E for Zn is comparatively lower why? means as compare to other transition element of same series.

Ans:— $Zn \rightarrow Zn^+ + e^-$. This is becoz Zn^+ with electronic configuration $3d^{10}4s^2$, $3d^{10}4s^1$, $3d^{10}4s^0$ will really loose 1 electron to acquire stable $3d^{10}$ configuration.

4) Oxidation State:— The transition elements have a tendency to show variable oxidation state.

Why?— becoz of tendency of penultimate d-electrons to enter into chemical bond formation in addition to ns as the energies of $(n-1)d$ & ns orbitals are comparable. Oxidation States 1st ↑ till middle due to unpaired e^- then ↓ due to paired.

• Oxidation states of 1st row of transition metals:—

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

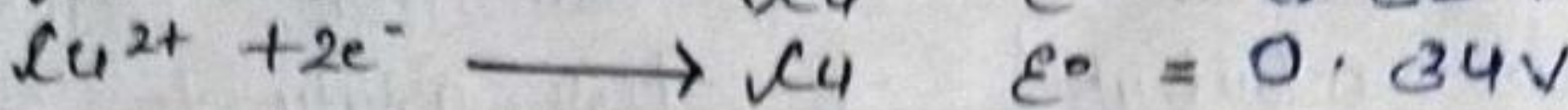
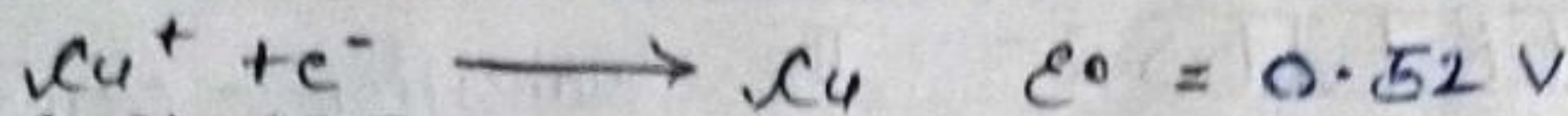
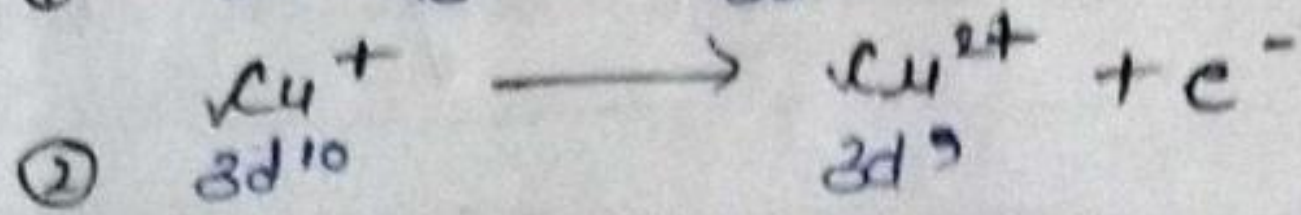
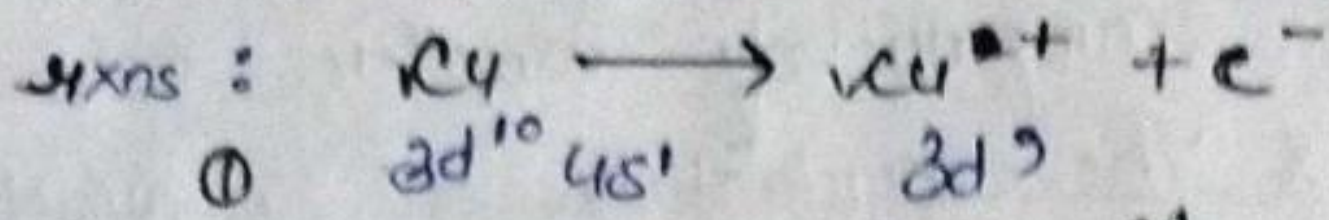
• Maximum value of oxidation state for any transition is found in its compounds with F & O as they are the most electronegative elements of periodic table.

Qus: Phosphorus & Vanadium both exhibit variable O.S but due to different reasons Explain?

Ans: Phosphorus: due to inert pair effect.

Vanadium: transition element participation of d-orbital electron.

• Stability of an oxidation no is also determined with the help of electrode potential values.



ie, Cu^{2+} is more stable than Cu^{+} as compare to $E^{\circ} \text{Cu}^{2+}/\text{Cu} < E^{\circ} \text{Cu}^{+}/\text{Cu}$ tendency of Cu^{2+} to undergo reduction is less.

• Mo (VI) & W (VI) are found to be more stable than Cu (VII). Thus, Cu(VII) is the form of dichromate in acidic medium is a strong oxidising agent whereas MoO_3 & WO_3 are not.

5) Magnetic Properties :-

When a magnetic field is applied to substances

mainly 2 types of magnetic behaviour are observed :-

• **Diamagnetism** :- repelled by the applied field.

• **Paramagnetism** :- attracted by the applied field.

→ Paramagnetism arises from the presence of unpaired electrons, each such electrons having a magnetic moment associated with its spin angular momentum & orbital angular momentum.

→ The transition elements with unpaired electrons will show paramagnetic characters.

For the 1st transition series, the magnetic moment can be calculated by using

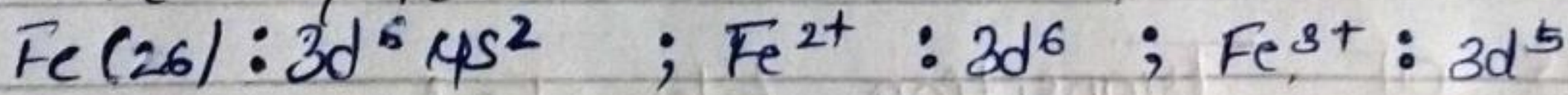
spin formula only $M = \sqrt{n(n+2)}$ B.M unit (Bohr Magneton), • Due to spinning of electrons about their own axis.

n :- no. of unpaired electrons.

Note :- Greater the no. of unpaired electrons more is the paramagnetic nature.

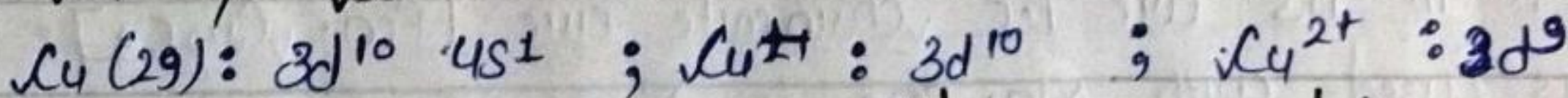
Qus: Compare the magnetic characteristics of following :-

Ans: (i) Fe^{2+} & Fe^{3+}



Fe^{3+} with greater no. of unpaired e^{-} is more paramagnetic.

(ii) Cu^{+} & Cu^{2+}



diamagnetic as all electrons are paired

weakly paramagnetic as only 1 e^{-} are unpaired.

6) Formation of coloured ions :-

Transition elements are coloured becoz when an electron from a lower energy orbital is excited to a higher energy d-orbital with d subshell then the energy of excitation lies in the visible region & the corresponding complementary colour is observed.

Note :- Transition elements are coloured becoz of d-d transition which

is possible becoz the degeneracy of d orbitals is destroyed in presence of anions called ligands.

• The frequency of the light absorbed is determined by the nature of the ligand.

7) Formation of complexes :- The transition metals form a large no. of complex compound due to comparatively smaller sizes of the metals ions, their high ionic charges & the availability of d-orbitals for bond formation.

8) CATALYTIC PROPERTIES :- The transition elements show catalytic activity which can be attributed to their ability to show variable oxidation states & their tendency to form complexes.

Eg:- V_2O_5 in contact process, finely divided iron in Haber's process.

9) ALLOY FORMATION :- The transition elements are able to form alloy i.e. homogeneous mixture of 2 or more atoms becoz of their similar radii due to which they are able to mutually substitute one another in their crystalline lattice. The alloys so formed are hard & have often high melting points.

10) Formation of Interstitial compounds :- Transition elements are able to form interstitial compounds when small atoms like H, C or N are trapped inside the crystal lattice of metals.

* Interstitial compounds :- Usually non stoichiometric neither typically ionic nor covalent the principal physical & chemical compound.

(a) They have high melting points, higher than those of pure metals.

(b) They are very hard, some bauxides approach diamond in hardness.

(c) They retain metallic conductivity. Bauxides means binary compound of bauxon.

(d) They are chemically inert. Eg:- Mn_4N , Fe_3H , $TiH_{1.7}$ etc

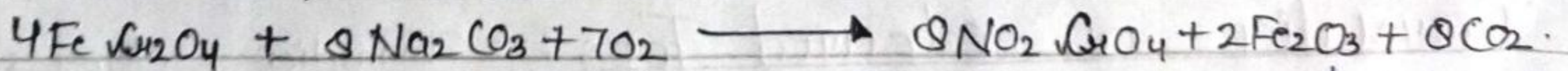
* Complex compound :- Complex compounds are those in which the metal ions bind a no. of anions or neutral molecules giving complex species with characteristic properties. Eg:- $[Fe(CN)_6]^{3-}$, $[Cu(NH_3)_4]^{2+}$ etc..

Important compounds of Transition Elements :-

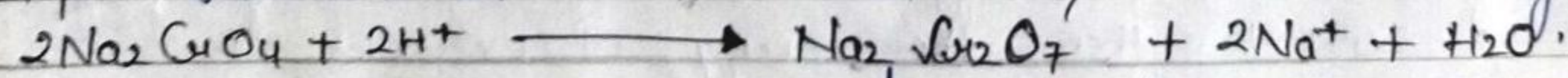
1. Potassium Dichromate $[K_2Cr_2O_7]$:-

• Preparation :- Obtained from its ore i.e. chromite ore $[FeO \cdot Cr_2O_3]$.

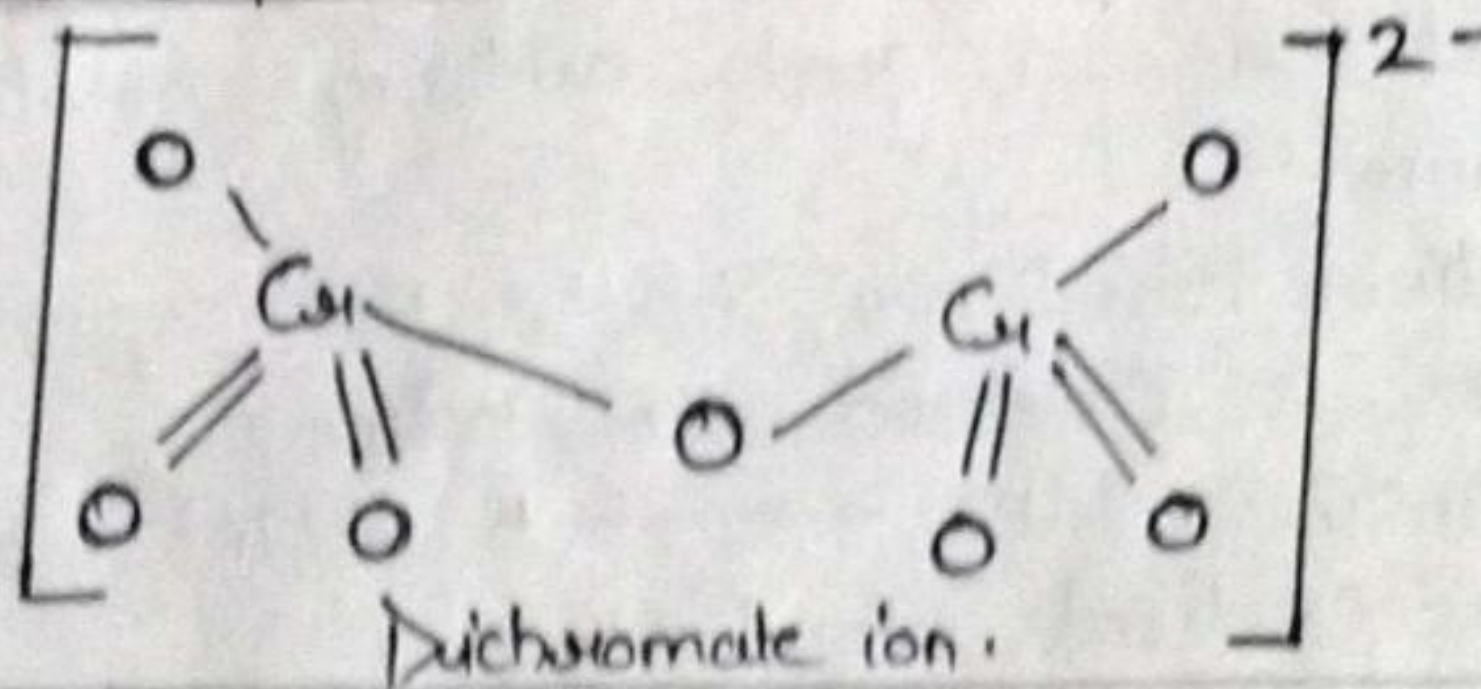
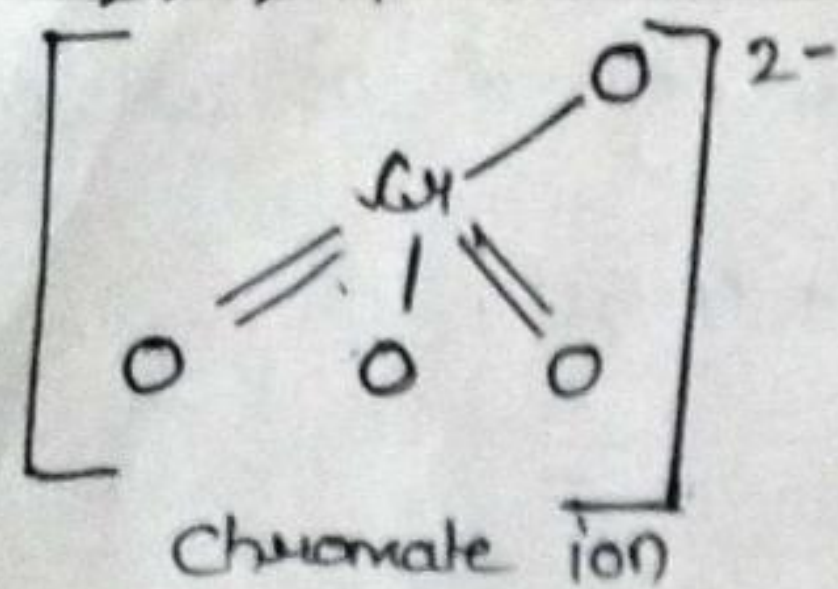
Step 1 :- The chromite ore is fused with Na_2CO_3 in presence of oxygen when it gives yellow coloured solⁿ of sodium chromate.



Step 2 :- Chromate solⁿ is then acidified (yellow) to form orange coloured dichromate solⁿ



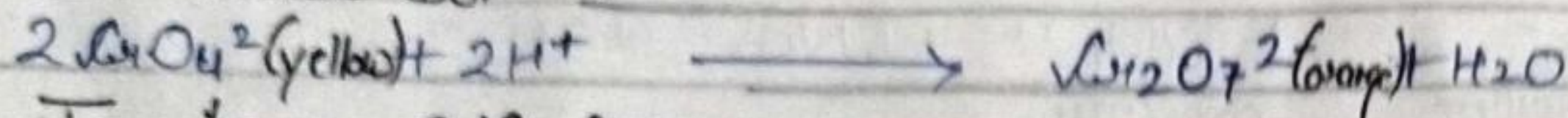
Step 3 :- $Na_2Cr_2O_7$ is then treated with KCl when it generates orange crystals of $K_2Cr_2O_7$.



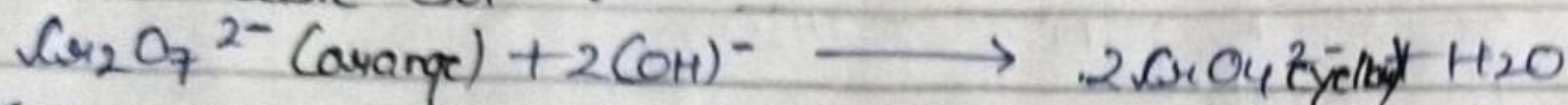
Properties :-

(i) Chromate & Dichromate ions are interconvertible depending upon the pH of the salts.

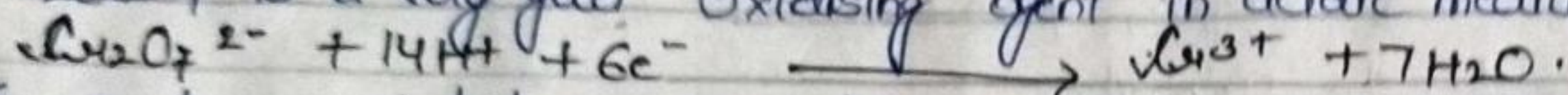
(a) In acidic solⁿ :-



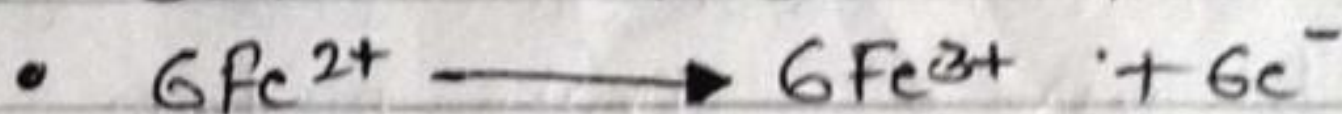
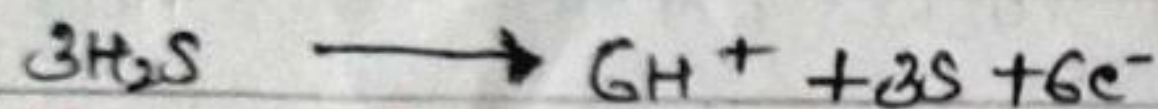
(b) In basic solⁿ :-



(ii) $K_2Cr_2O_7$ is a very good oxidising agent in acidic medium & it is reduced to Cr^{3+} .



It oxidises iodides to iodine, sulphides to sulphur, stannous to stannic & ferrous to ferric.



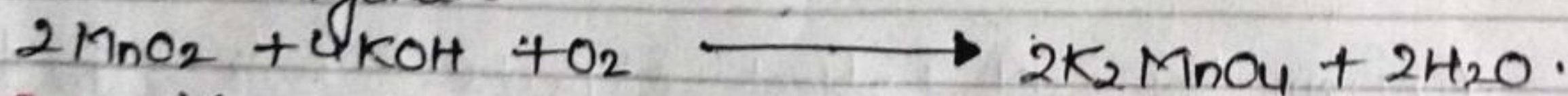
Uses of $K_2Cr_2O_7$:-

- Used as a primary standard in volumetric analysis.
- Used as an oxidant for oxidation of any organic compounds.
- Used in leather industry.
- Sodium dichromate has greater solubility in water is extensively used as an oxidising agent in organic chemistry.

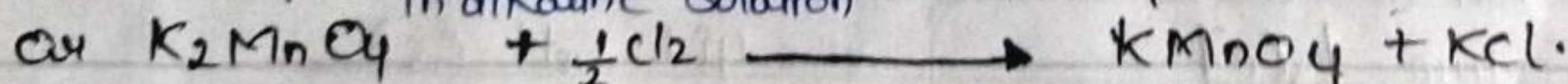
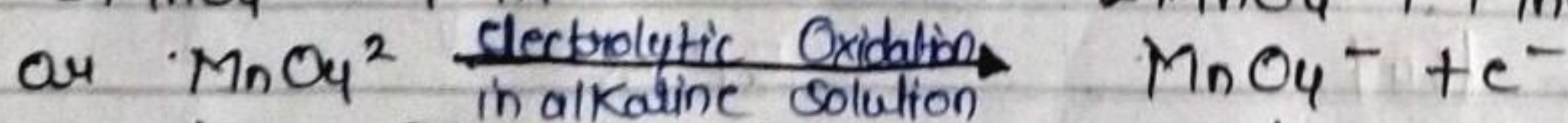
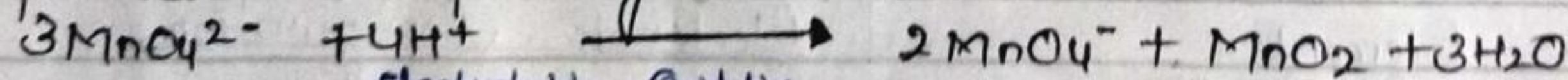
2) Potassium Permanganate $[KMnO_4]$:-

• Preparation :- Obtained from its ore pyrolusite i.e. MnO_2

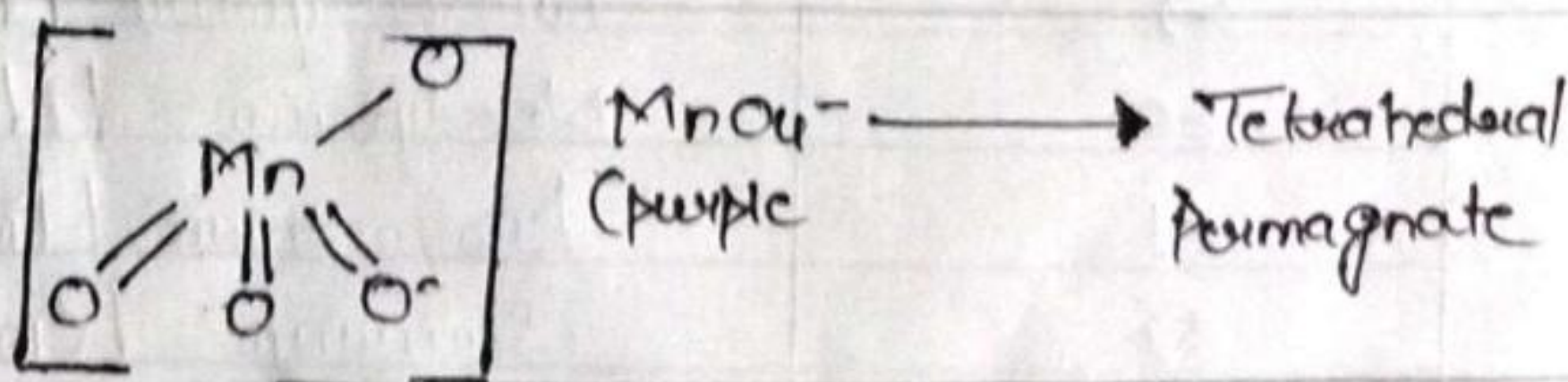
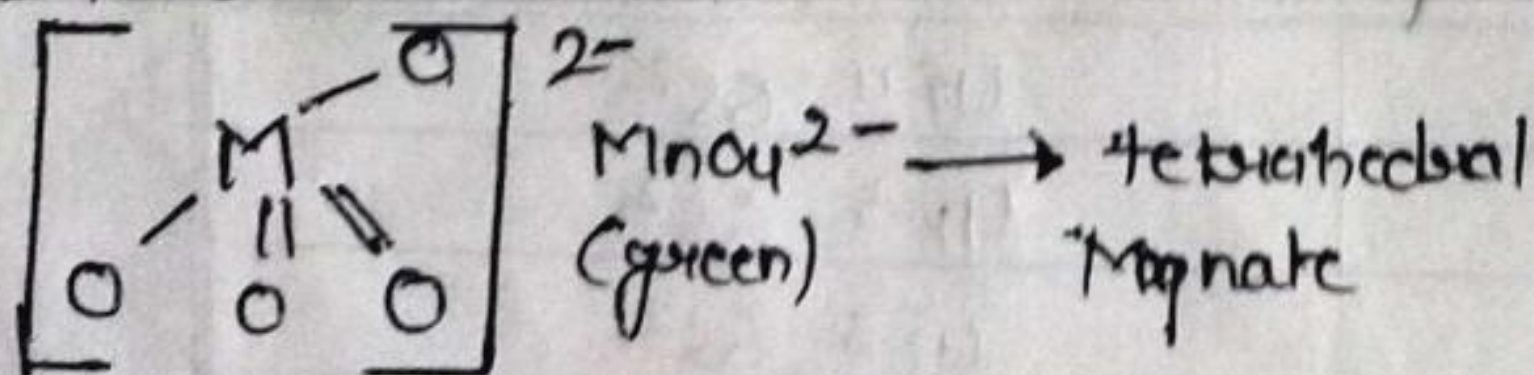
Step 1 :- MnO_2 is fused with KOH when it gives green coloured solⁿ of potassium manganate



Step 2 :- Manganate ion undergoes disproportionation in acidic medium to form purple coloured permanganate ion.

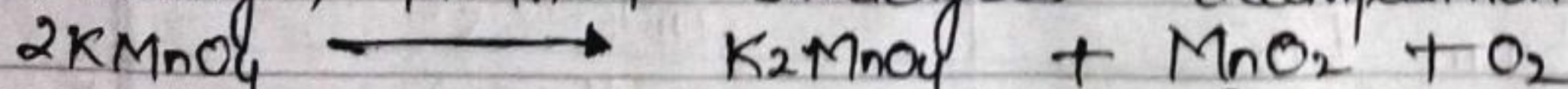


Structure :-



Properties :-

(i) On heating, $KMnO_4$ undergoes decomposition.



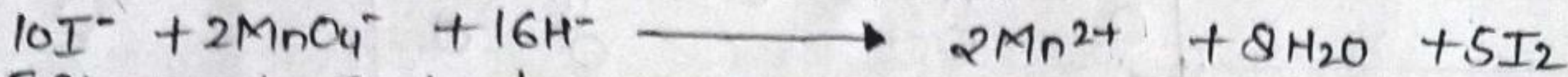
(ii) It has 2 physical properties of considerable interest :- its intense

colour & its weak temperature dependent paramagnetism.

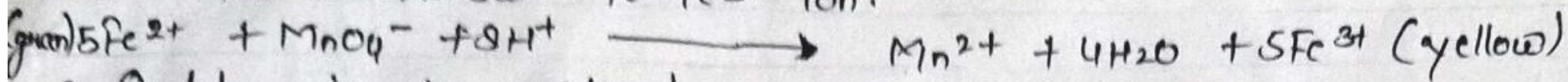
(ii) $KMnO_4$ acts as a good oxidising agent in acidic, neutral as well as alkaline medium.

(a) Acidic Medium :- $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$.

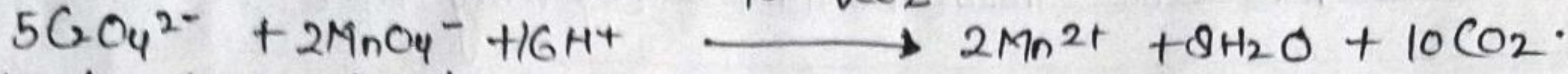
Eg :- Iodine is Oxidised to iodine.



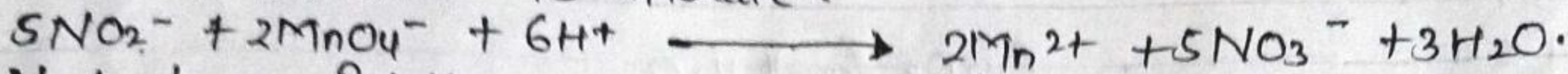
• Fe^{2+} ion is Oxidised to Fe^{3+} ion.



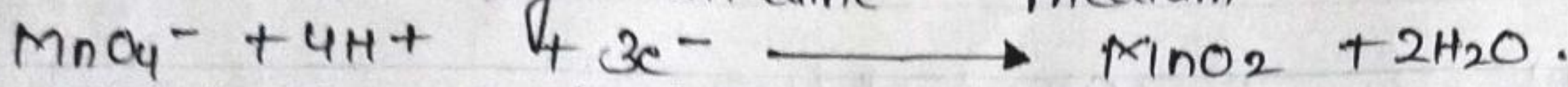
• Oxalate ion is Oxidised to CO_2



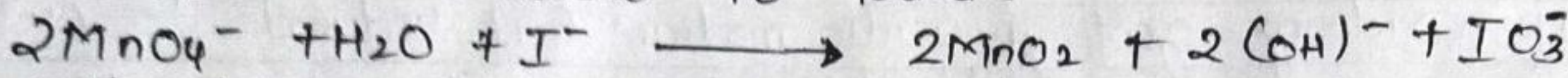
• Nitrate is Oxidised to nitrate.



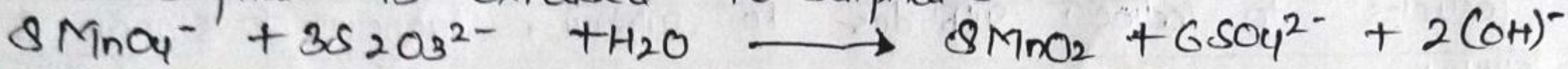
(b) Neutral or faintly alkaline medium



Eg :- Iodide is Oxidised to iodate



• Thio sulphate is Oxidised to sulphate



(c) In alkaline medium $MnO_4^- + e^- \longrightarrow MnO_4^{2-}$

Qus 1 In $KMnO_4$ titration with Mohr salt or oxalic acid, neither HNO_3 nor HCl can be used to make medium acidic why?

Ans :- HNO_3 is itself a good oxidising agent & hence will oxidise Fe^{2+} to Fe^{3+} .

HCl can't be used because $KMnO_4$ can easily oxidise Cl^- to Cl_2 .

Uses of $KMnO_4$:-

- Used in analytical chemistry.
- Used as a favorite oxidant in preparation organic chemistry.
- Used in bleaching of wool, cotton, silk & other textile fibres.
- Used for decolourisation of oils.

Qus 2 In which $KMnO_4$ is the Oxidising power max?

Ans In acidic medium becoz of more charge.

F-Block :- also called inner transition elements.

The general Electronic configuration of f-block elements :- $(n-2)f^{1-14} (n-1)d^{0-1} ns^2$

The Lanthanoids :- (4f orbitals is filled).

Atomic No.	Element	Electronic Configuration
57	Lanthanum [La]	$5d^1 6s^2$
58	Cerium [Ce]	$4f^1 5d^1 6s^2$
59	Praseodymium [Pr]	$4f^3 6s^2$
60	Neodymium [Nd]	$4f^4 6s^2$
61	Promethium [Pm]	$4f^5 6s^2$
62	Samarium [Sm]	$4f^6 6s^2$
63	Europium [Eu]	$4f^7 5d^1 6s^2$
64	Gadolinium [Gd]	$4f^7 6s^2$
65	Terbium [Tb]	$4f^9 6s^2$
66	Dysprosium [Dy]	$4f^{10} 6s^2$
67	Holmium [Ho]	$4f^{11} 6s^2$

68	Erbium [Er]	$4f^{12} 6s^2$
69	Thulium [Tm]	$4f^{13} 6s^2$
70	Ytterbium [Yb]	$4f^{14} 6s^2$
71	Lutetium [Lu]	$4f^{14} 5d^1 6s^2$

(1) General Electronic Configuration :- The general electronic configuration of Lanthanoids is electron shift b/w f & d depending upon the stability of electronic configuration. (As we move higher in energy levels, energy gap is decreasing & shifting of e^- is very much possible)

(2) Atomic & Ionic Sizes :- size decreases as effective nuclear charge increasing. The gradual & steady decrease in atomic ionic radii along the Lanthanoid series i.e. from La to Lu is called "Lanthanoid contraction".
 • It can be explained on the basis of poor shielding effect of f-orbitals due to which the effective nuclear charge increase regularly & hence the size decrease regularly.

Consequences of Lanthanoid contraction :- Due to Lanthanoid contraction 2nd & 3rd Transition series exhibit similar atomic radii.

For eg 2nd series \rightarrow same size $\begin{matrix} \text{Zr} \\ \text{Hf} \end{matrix}$ $\begin{matrix} \text{Nb} \\ \text{Ta} \end{matrix}$ same size.

Ques: Zirconium (Zr) & Hafnium (Hf) occur together in nature?? why?

Ans :- It is becoz due to LANTHANOID CONTRACTION the 2 elements have almost identical radii & hence occur together in nature.

(3) Oxidation States :- In lanthanoids, the most pre-dominant & stable oxidation state is +3.

For certain elements +2 & +4 also exist where it is accompanied with stable electronic configuration of half filled or fully filled 4f-orbitals.

Eg :- $\text{Eu}^{2+} : 4f^7$, $\text{Yb}^{2+} : 4f^{14}$, $\text{Ce}^{4+} : 4f^0$, $\text{Tb}^{4+} : 4f^7$

• Both +2 & +4 Oxidation state have a tendency to revert back to more stable Oxidation state of +3.

• Therefore Eu^{2+} & Yb^{2+} have a tendency to undergo oxidation to +3 Oxidation state & hence, act as reducing agent.

• Likewise Ce^{4+} & Tb^{4+} have a tendency to undergo reduction to +3 Oxidation state & hence, act as Oxidising agent.

Note :- Ce^{4+} is such a good oxidising agent that it can even oxidise water, still it is used as an oxidising agent of H_2O by Ce^{4+} is kinetically very slow process.

(4) General Characteristics :- All the lanthanoids are silvery white soft metals & tarnish rapidly in air.

• The Hardness increases with increasing atomic no. Samarium being steel hard.

• Their melting points range b/w 1000 to 1200 K But Samarium melts at 1623 K.

• They have typical metallic structure & are good conductors of heat & electricity.

- City.

Lanthanoids also exhibit colour.

Colour: - Make trivalent lanthanoid ions are coloured both in the solid state & in aqueous solutions due to the presence of electrons.
 $\text{Lu}^{3+} : 4f^{14}$, $\text{Yb}^{2+} : 4f^{14}$, $\text{Ce}^{4+} : 4f^0$:- are colourless becoz of no f-f transition possible.

(5) **Magnetic Properties** :- Lanthanoids with unpaired electrons in f-orbital are going to exhibit paramagnetism.
• The paramagnetism rises to maximum in NEODYMIUM.

(6) **Chemical Properties** :-

- The metals combine with hydrogen when gently heated in gas.
- The carbides, Ln_3C , Ln_2C_3 & LnC_2 are formed when the metals are heated with carbon.
- They liberate H_2 from dilute acids & burn in halogens to form halides.
- They form oxides M_2O_3 & hydroxides M(OH)_3 .

Ques: - The basic character of hydroxides of Lanthanoids $[\text{M(OH)}_3]$ decrease along the La series why?

Ans: - It is becoz the size of the elements decreases due to Lanthanoid contraction & hence, the bond is difficult to break.

(7) **Uses of Lanthanoids** :- The best single use of Lanthanoids is for the production of alloy steels for plates & pipes.

MISCH METAL :- It is an alloy of Lanthanoid metal (25%) & iron (75%) with traces of S, C, Ca & Al.

Use of Misch metal :- It is used in Mg-based alloy to produce bullets, shell & lighter flint.

The ACTINOIDS :- (5f orbital is filled).

Atomic No.	Element	Electronic Configuration
89	Actinium [Ac]	$6d^2 7s^2$
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	Berkelium [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	Mendelevium [Md]	$5f^{13} 7s^2$
102	Nobelium [No]	$5f^{14} 7s^2$
103	Lawrencium [Lr]	$5f^{14} 6d^1 7s^2$

- The actinoids are radioactive elements.
- The latter members could be prepared only in microgram quantities.
- These facts render their study more difficult.

(1) General Electronic Configuration :- $5f^{1-14} 6d^{0-1} 7s^2$

The irregularities are related to the stabilities of f_0, f_7, f_{14} occupancies of the $5f$ orbitals.

(2) Ionic Sizes :- Along the actinoid series, the size of atoms or M^{3+} ions decreases gradually & is referred to as the Actinoid contraction.

(3) Oxidation States :- They show a wider range of oxidation state which is partly attributed to the fact that the $5f, 6d$ & $7s$ levels are of comparable energies.

- The actinoids show in general +3 oxidation state.

(4) General Characteristics :- The actinoid metals are all silvery in appearance but display a variety of structures due to irregularities in metallic radii.

- The actinoids are highly reactive metals.