

—: 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 d 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] [Hafnium] Hf(72) ↔ (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 \downarrow in metallic / atomic radius coupled with \uparrow in atomic mass results in \uparrow in density ($\rho = \frac{m}{V}$).

3) Ionisation Enthalpy: — Due to \uparrow in nuclear charge, there is an \uparrow 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.

	$I.E_1 + I.E_2$	$I.E_1 + I.E_2 + I.E_3 + I.E_4$ (Jmol ⁻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.

Ques 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.

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

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

Ques 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 \uparrow till middle due to unpaired e^{-} then \downarrow 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					

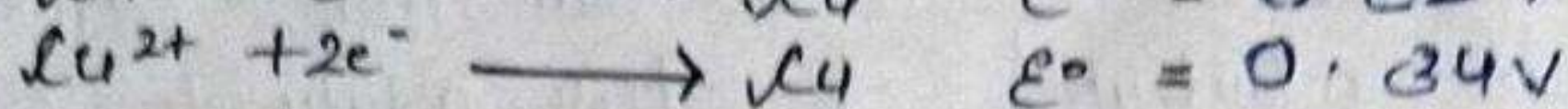
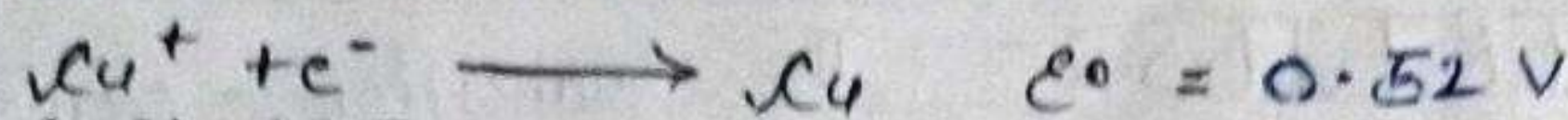
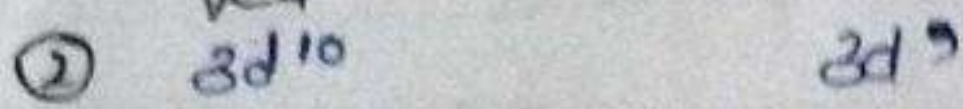
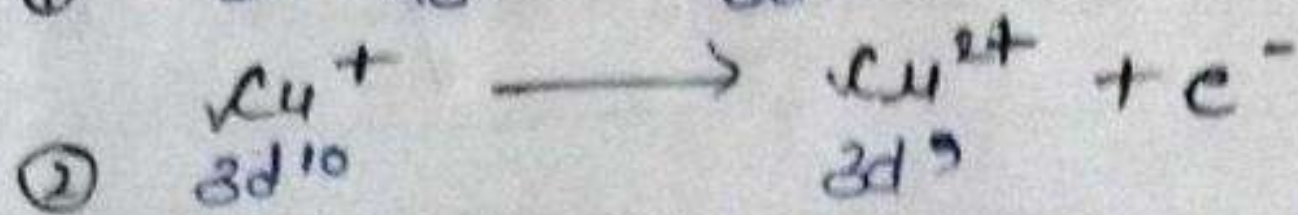
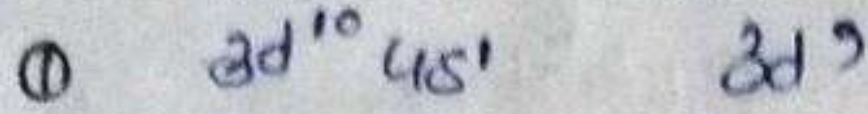
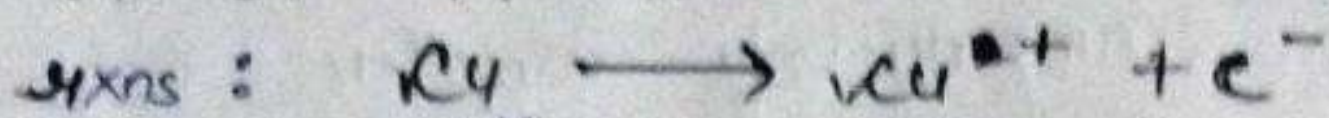
- Maximum value of oxidation state for any transition is found in its compounds with F & O as they are the most electronegative elements of periodic table.

Ques 1 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.



i.e., 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 character.

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

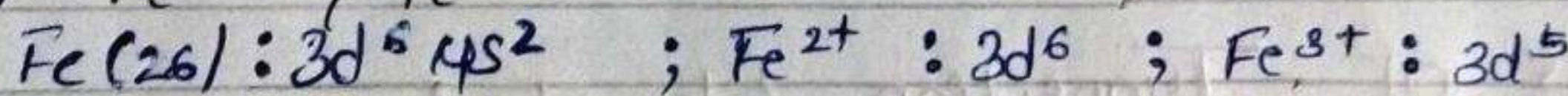
Spin Formula only $M = \sqrt{n(n+2)}$ B.M unit (Bohr Magneton), • Due to spinning of electrons about their own axis.

n:- no. of unpaired electrons.

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

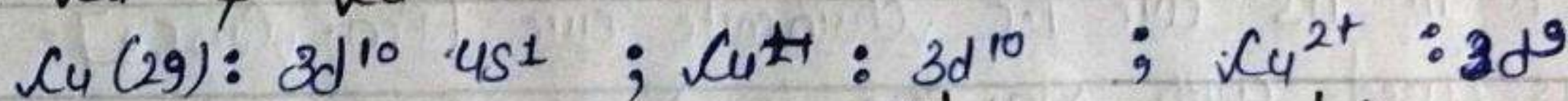
Ques 2: Compare the magnetic characteristics of following :-

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 within 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 boron.
- (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 $[FeO \cdot Cr_2O_3]$.

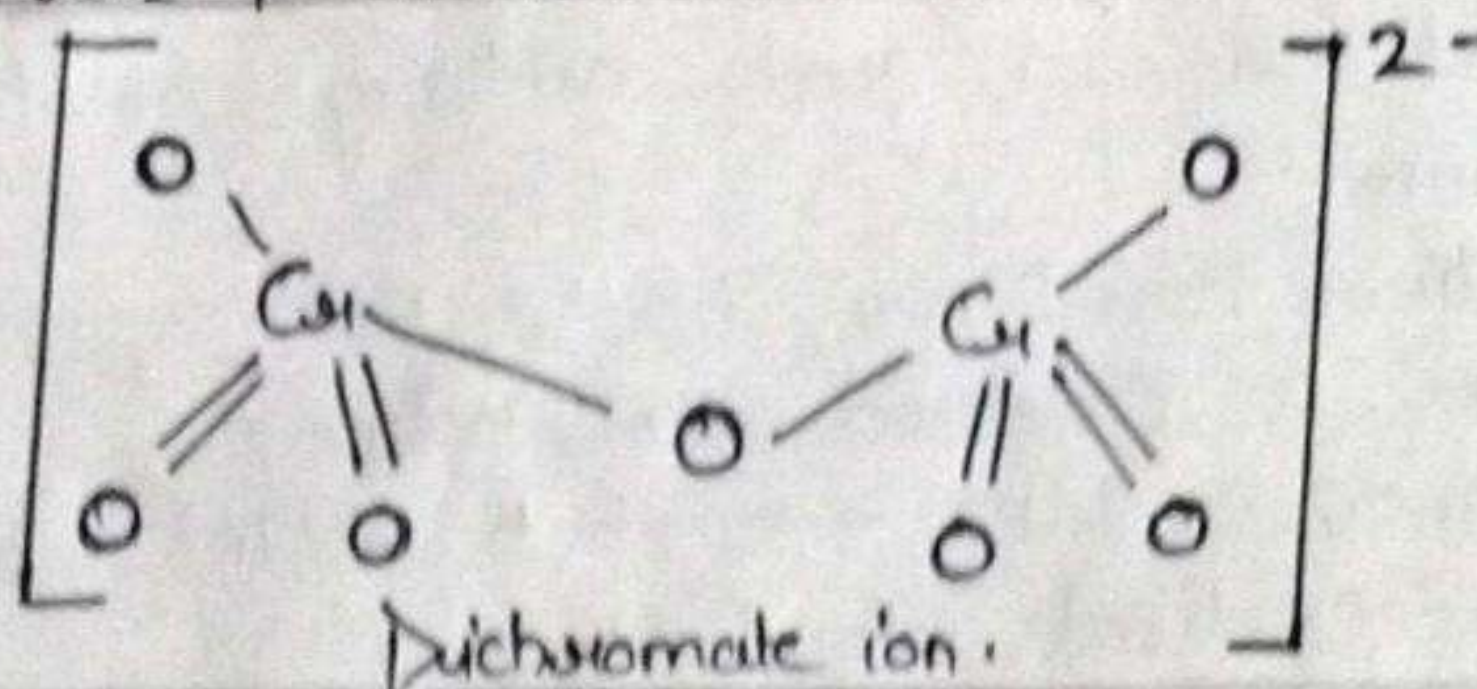
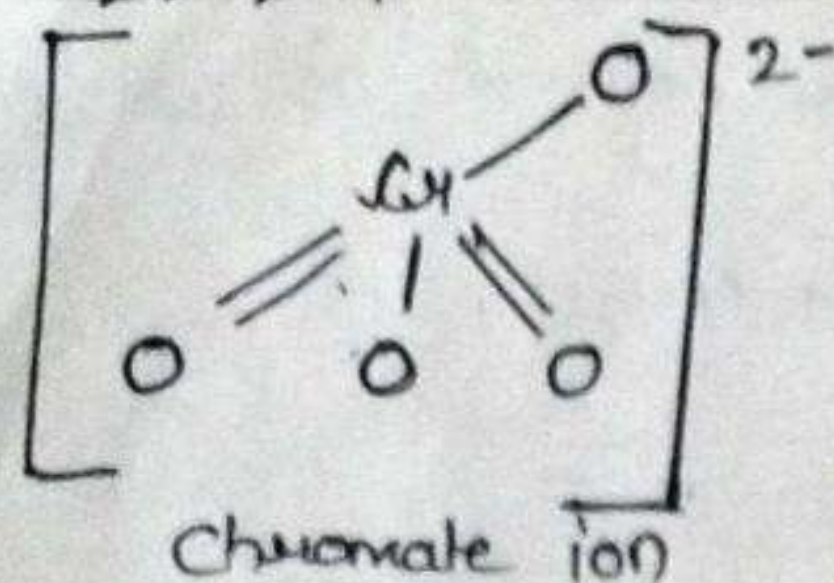
Step 1 :- The chromite ore is fused with Na_2CO_3 in presence of oxygen when it gives yellow coloured solⁿ of sodium chromate.



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



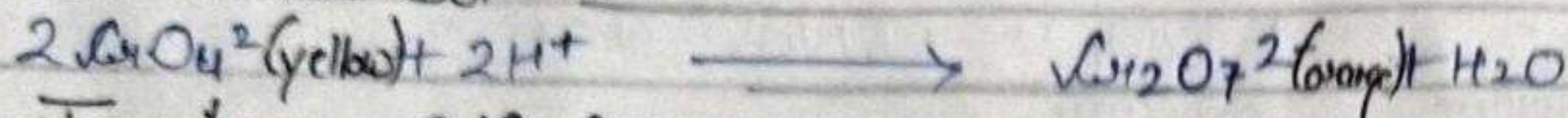
Step 3 :- $Na_2Cr_2O_7$ is then treated with KCl when it generates orange crystals of $K_2Cr_2O_7$.



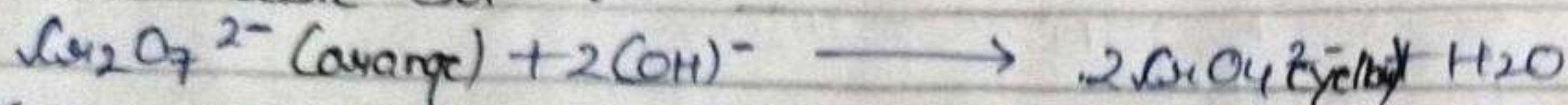
Properties :-

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

(a) In acidic solⁿ :-



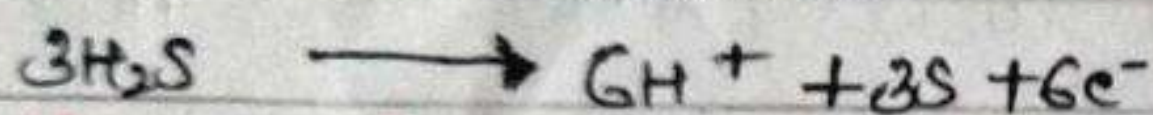
(b) In basic solⁿ :-



(ii) $\text{K}_2\text{Cr}_2\text{O}_7$ 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.



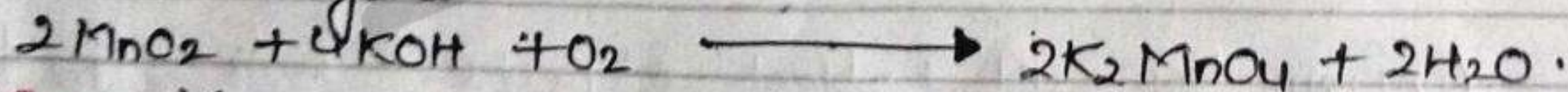
Uses of $\text{K}_2\text{Cr}_2\text{O}_7$:-

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

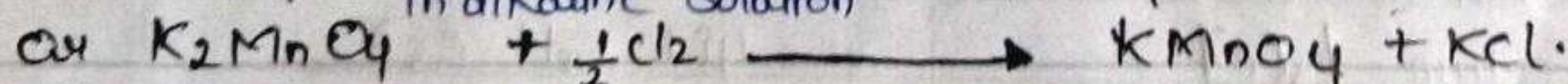
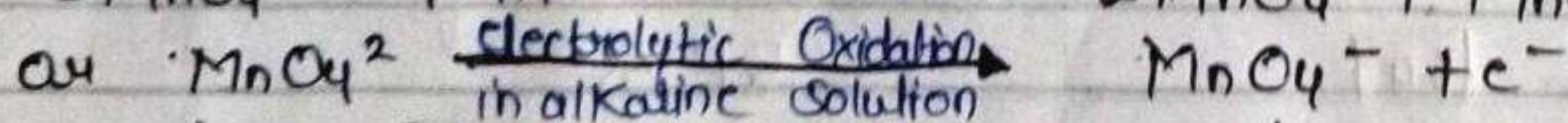
2) Potassium Permanganate $[\text{KMnO}_4]$:-

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

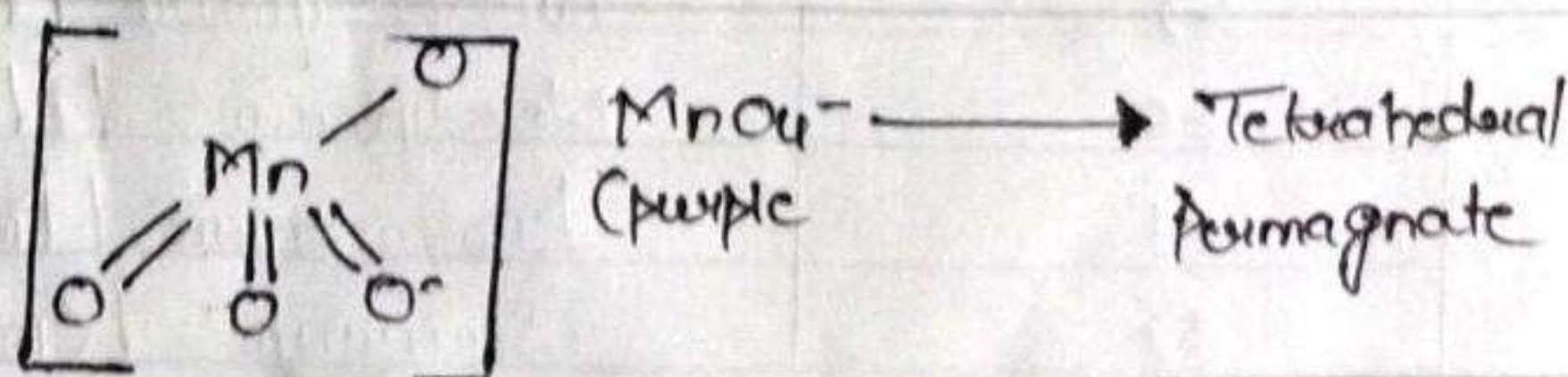
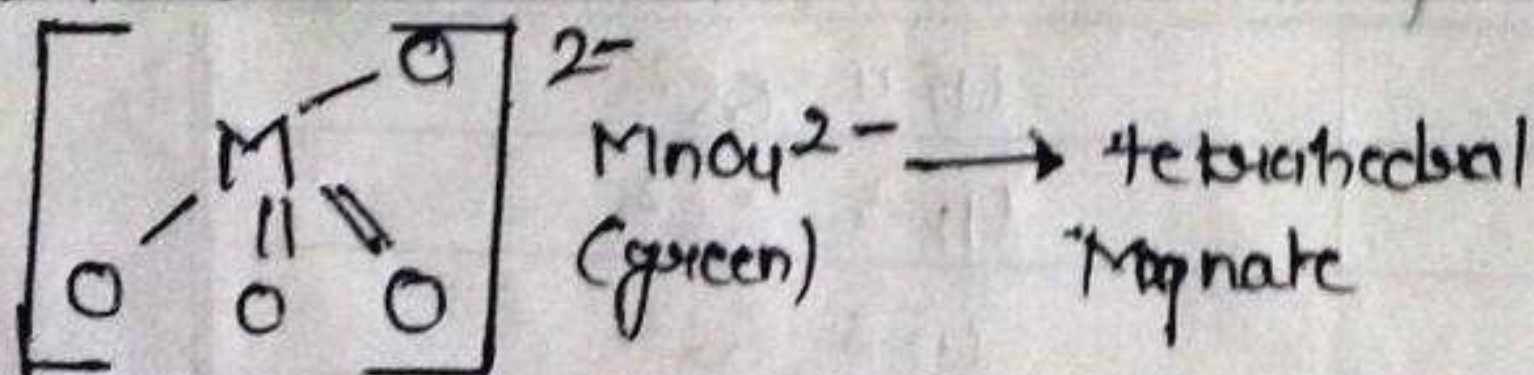
Step 1 :- MnO_2 is fused with KOH when it gives green coloured solⁿ of potassium manganate



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

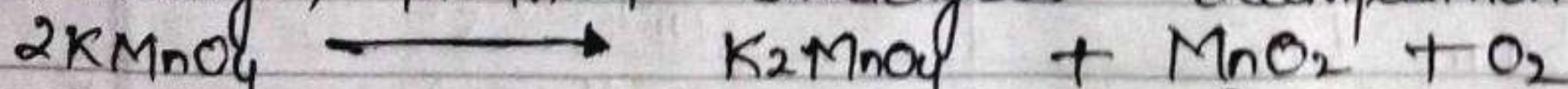


Structure :-



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.

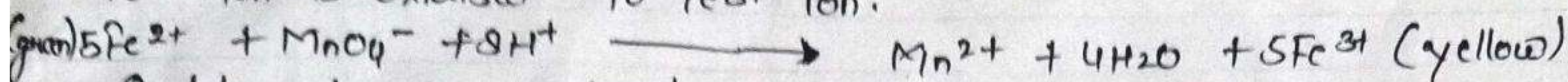
(ii) KMnO_4 acts as a good oxidising agent in acidic, neutral as well as alkaline medium.

(a) Acidic Medium :- $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$.

Eg :- Iodine is Oxidised to iodine.



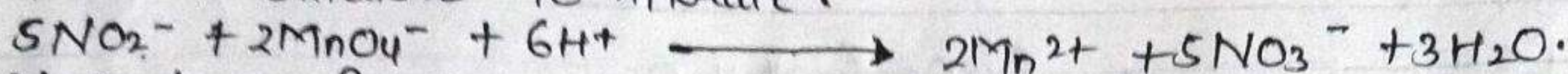
• Fe^{2+} ion is Oxidised to Fe^{3+} ion.



• Oxalate ion is Oxidised to CO_2



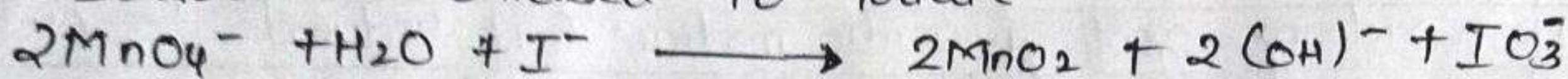
• Nitrate is Oxidised to nitrate.



(b) Neutral or faintly alkaline medium



Eg :- Iodide is Oxidised to iodate



• Thiosulphate is Oxidised to sulphate



(c) In alkaline medium $\text{MnO}_4^- + \text{e}^- \longrightarrow \text{MnO}_4^{2-}$

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 powerful 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]	$4f^{11} 6s^2$
		$4f^{12} 6s^2$

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 increases regularly & hence the size decreases 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.
 3rd series \rightarrow

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

Ans :- It is because 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.

d) They form oxides M_2O_3 & hydroxides $\text{M}(\text{OH})_3$.

Ques:- The basic character of hydroxides of Lanthanoids $[\text{M}(\text{OH})_3]$ 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 nanogram 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.