

LIVE

# d-BLOCK

for JEE-MAIN

One Shot

By VJ Sir

7:30 PM Tonight 🔥

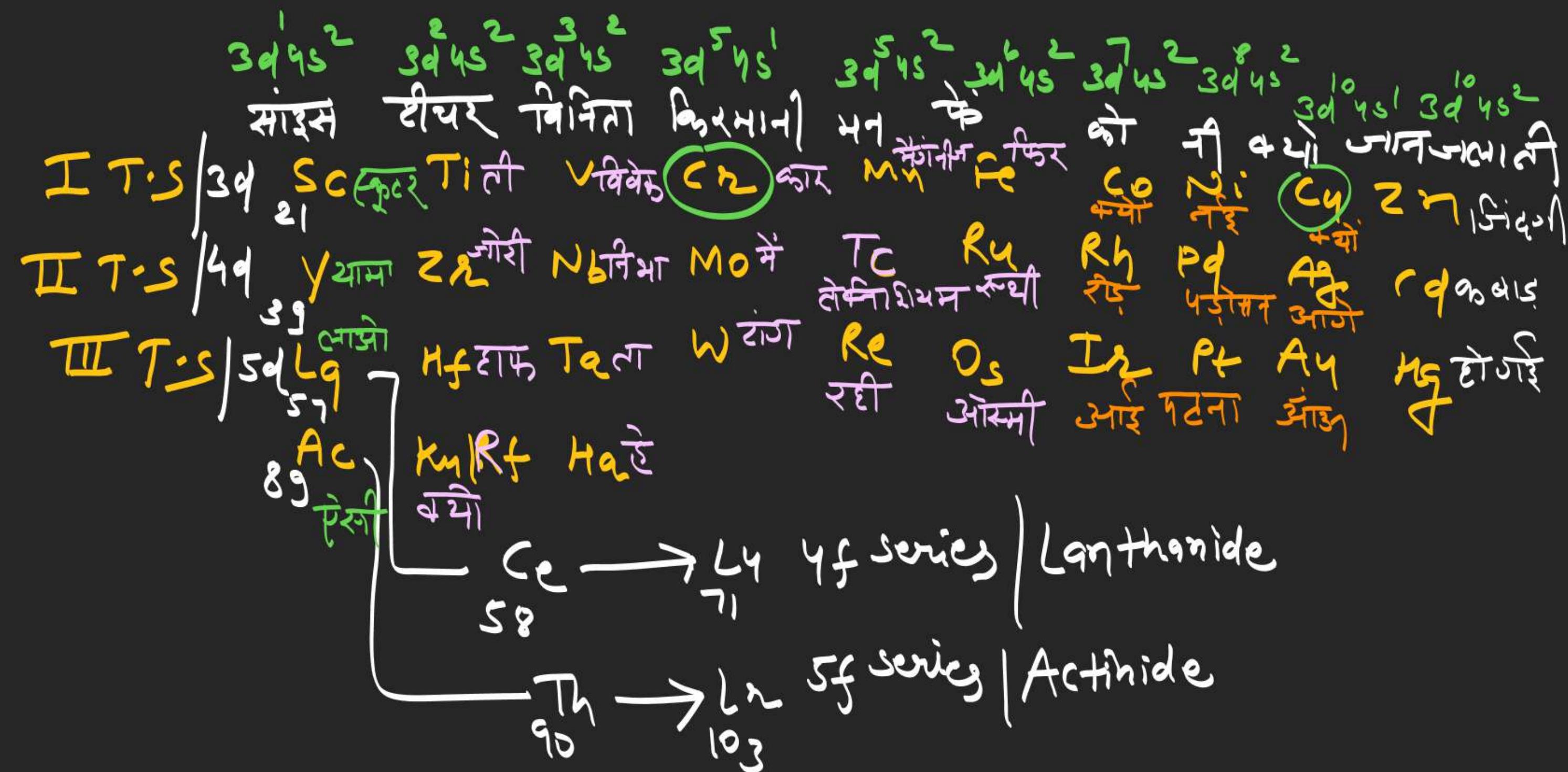
Apni Kaksha

A

**d -BLOCK****TRANSITION ELEMENTS**

**Definition:** They one often called 'transition elements' because their position in the periodic table is between s-block and p-block elements. Typically, the transition elements have an incompletely filled d-level, are not considered as transition elements but they are d-block elements. Since Zn group has  $d^{10}$  configuration in their ground state as well as in stable oxidation state, they are not considered as transition elements but they are d-block elements.

<b>1st SERIES</b>									
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Z	21	22	23	24	25	26	27	28	29
4 s	2	2	2	1	2	2	2	2	1
3 d	1	2	3	5	5	6	7	8	10



**d -BLOCK**

2nd SERIES									
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Z	39	40	41	42	43	44	45	46	47
5 s	2	2	1	1	1	1	1	0	1
4 d	1	2	4	5	6	7	8	10	10

3rd SERIES									
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au
Z	57	72	73	74	75	76	77	78	79
6 s	2	2	2	2	2	2	2	1	1
5 d	1	2	3	4	5	6	7	9	10

4th SERIES									
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg
Z	89	104	105	106	107	108	109	110	111
7 s	2	2	2	2	2	2	2	2	1
5 d	1	2	3	4	5	6	7	8	10

## d -BLOCK

**General Characteristics:**

(i) **Metallic character:** They are all metal and good conductor of heat & electricity

(ii) **Electronic configuration:**  $(n-1)d^{1-10} ns^{1-2}$

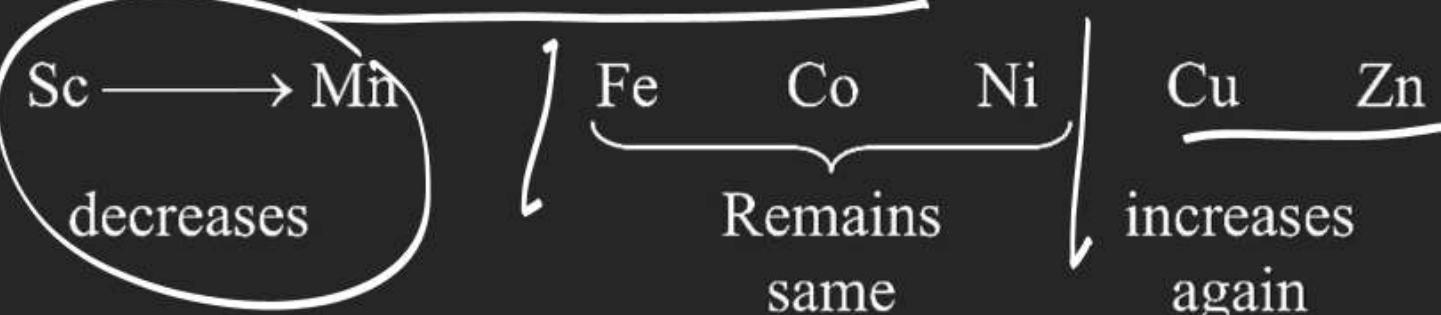


(iii) **M.P.**

Cr }  $\rightarrow$  Maximum  
 Mo } 6 no. of unpaired e<sup>-</sup>s  
 W } Are involved in metallic bonding

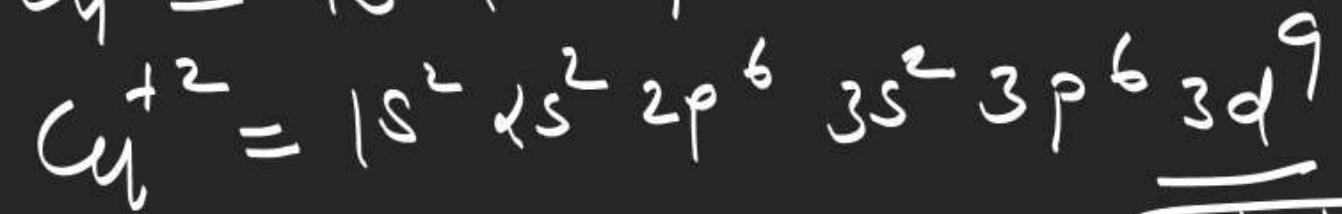
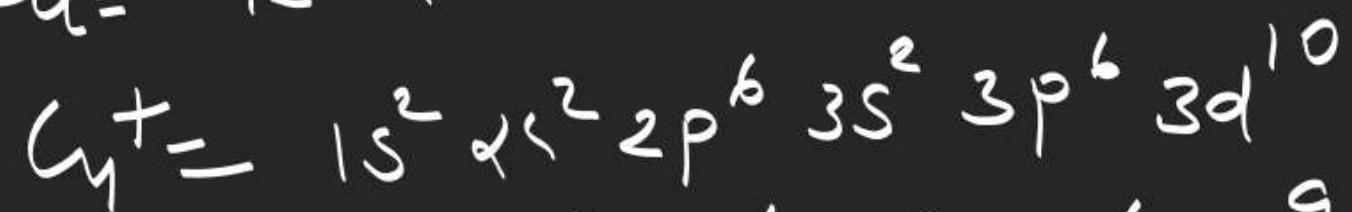
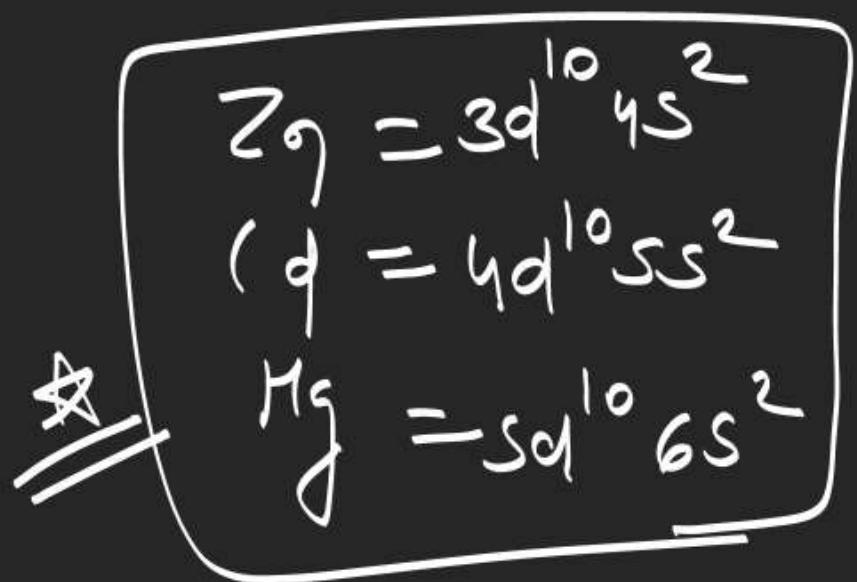
Zn } Lowest m.p.  
 Cd } Due to no unpaired e<sup>-</sup>  
 Hg } For metallic bonding

(iv) **Variation in atomic radius:**



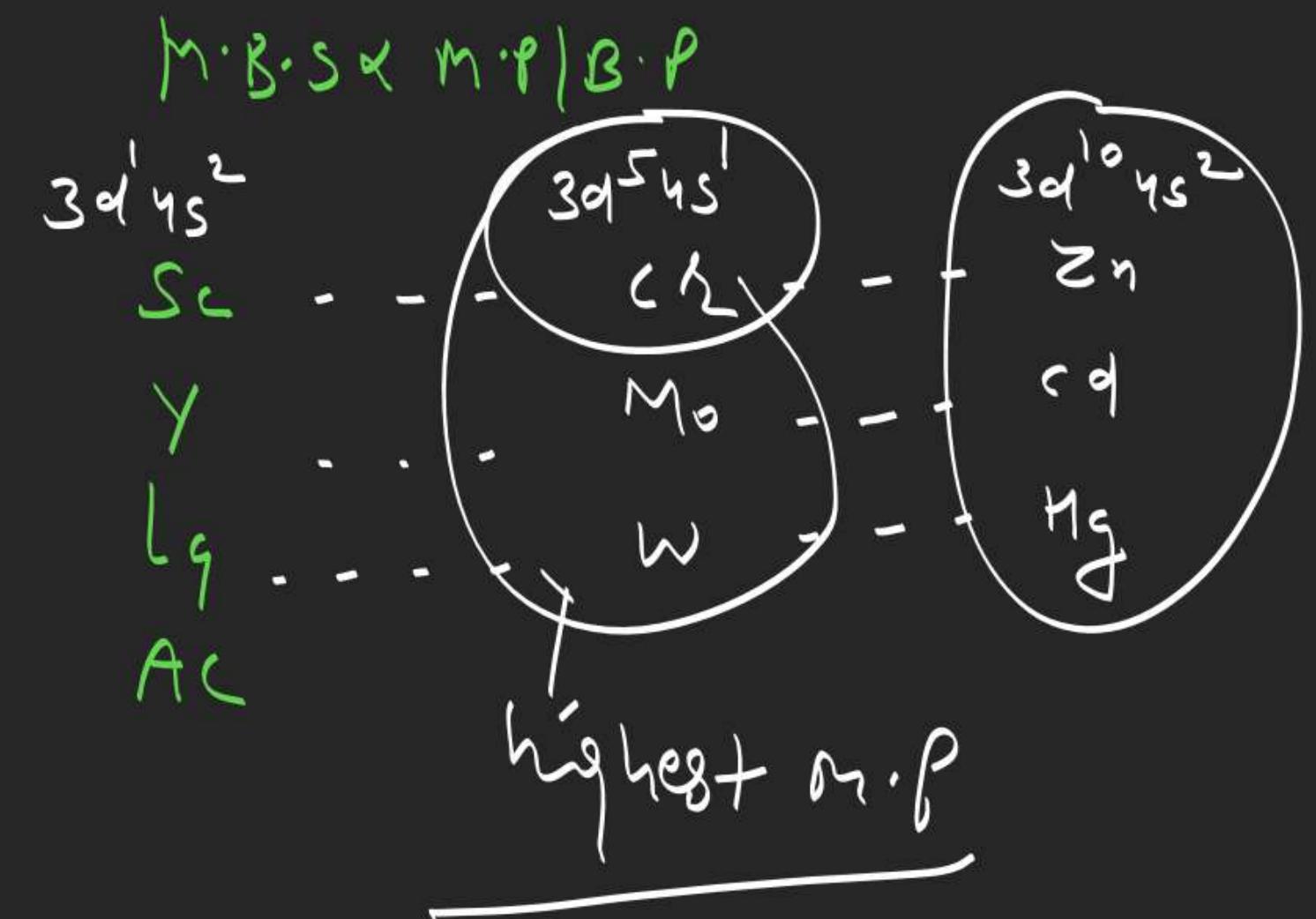
d-block | Transition element

d-block element which have partial filled d-orbital in Cr's or in stable oxidation state



7L	7L	7L	7L	7
----	----	----	----	---

M.B.S  $\propto$  unpaired  $e^-$



Ques

Which of the following  
element can use as  
filament in bulb

- ① Fe ② Zn ~~③~~ Mo ④ all

## d -BLOCK

(v) Ionisation energy:

1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, IE, s are increasing from left to right for 1<sup>st</sup> Transition series, but

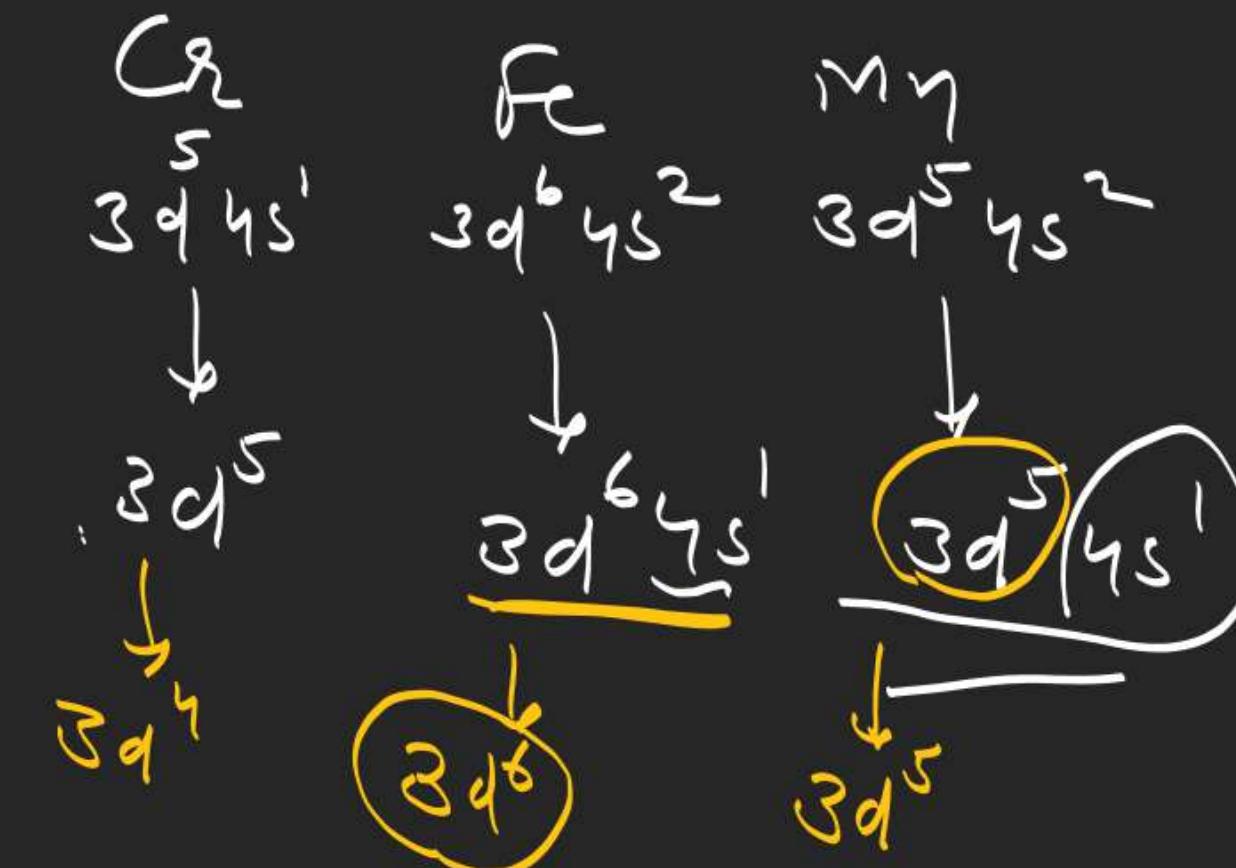
not regularly.



For 2<sup>nd</sup> IE Cr > Fe > Mn and Cu > Zn



For 3<sup>rd</sup> IE Mn > Cr > Fe and Z has highest



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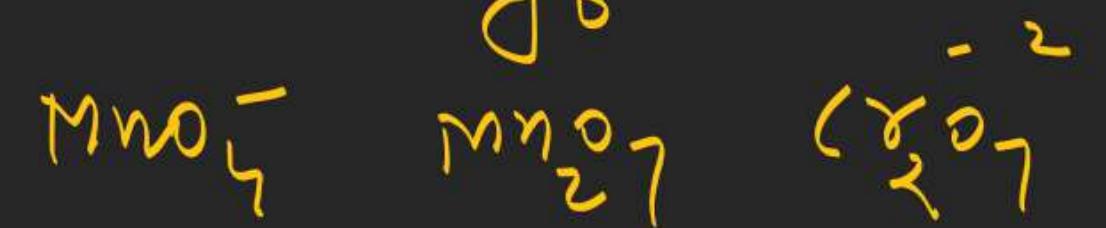
Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Atomic number	21	22	23	24	25	26	27	28	
Electronic configuration	M	3d <sup>1</sup> 4s <sup>2</sup>	3 d <sup>2</sup> 4 s <sup>2</sup>	3 d <sup>3</sup> 4 s <sup>2</sup>	3d <sup>5</sup> 4s <sup>2</sup>	3 d <sup>5</sup> 4 s <sup>2</sup>	3d <sup>6</sup> 4s <sup>2</sup>	3d <sup>7</sup> 4s <sup>2</sup>	3 d <sup>10</sup> 4 s <sup>2</sup>
	M <sup>+</sup>	3 d <sup>1</sup> 4 s <sup>1</sup>	3 d <sup>2</sup> 4 s <sup>1</sup>	3d <sup>3</sup> 4s <sup>1</sup>	3 d <sup>5</sup>	3d <sup>5</sup> 4s <sup>1</sup>	3d <sup>6</sup> 4s <sup>1</sup>	3 d <sup>7</sup> 4 s <sup>1</sup>	3 d <sup>8</sup> 4 s <sup>1</sup>
	M <sup>2+</sup>	3 d <sup>1</sup>	3 d <sup>2</sup>	3 d <sup>3</sup>	3 d <sup>1</sup>	3 d <sup>5</sup>	3 d <sup>6</sup>	3 d <sup>7</sup>	3 d <sup>8</sup>
	M <sup>3+</sup>	[Ar]	3 d <sup>1</sup>	3 d <sup>2</sup>	3 d <sup>3</sup>	3 d <sup>1</sup>	3 d <sup>5</sup>	3 d <sup>6</sup>	3 d <sup>7</sup>
Enthalpy of atomization <u>Δ<sub>1</sub>H<sup>⊖</sup>/kJmol<sup>-1</sup></u>	326	473	515	397	281	416	425	430	
Ionisation Enthalpy, Δ <sub>1</sub> H <sup>⊖</sup> /kJ mol <sup>-1</sup>	I	631	656	650	653	717	762	758	736
Δ <sub>1</sub> H <sup>⊖</sup>	II	1235	1309	1414	1592	1509	1561	1644	1752
	III	2393	2657	2833	2990	3260	2962	3243	3402

**VARIABLE OXIDATION STATES POSSIBLE:**

- (1) **The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7 .**
- (2) **The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc,Ti) or too many d electrons (hence fewer orbitals available in which to share electrons with others) for higher valence ( Cu,Zn).**
- (3) **Thus, early in the series scandium(II) is virtually unknown and titanium (IV) is more stable than Ti(III) or Ti(II).**
- (4) **At the other end, the only oxidation state of zinc is +2 (no d electrons are involved).**

Oxidation state  $\Rightarrow$  (i) higher O.S  $\left[ +4 +5 +6 +7 +8 \right]$   
 (ii) Common O.S  $\left[ +2 +3 \right]$   
 (iii) lower O.S  $\left[ -1 0 +1 \right]$

Higher O.S  $\rightarrow$  it is found in  
oxides    fluorides  
 and oxyfluoride



F and oxygen both are strong oxidising agent due to their small size and higher E.N.

Common O.S → +2 +3

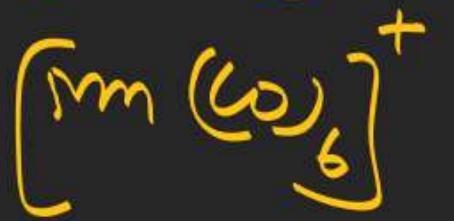
more common = +3

it is found in their sulphide and chlorides



Lower O.S. = (-1 - 0 + 1) it is found in

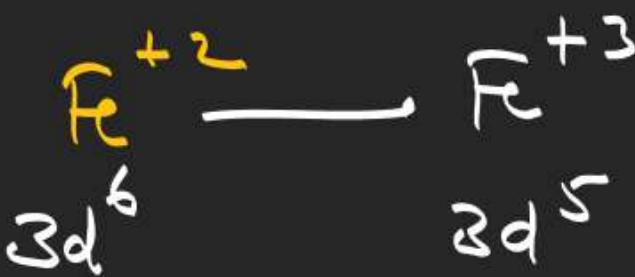
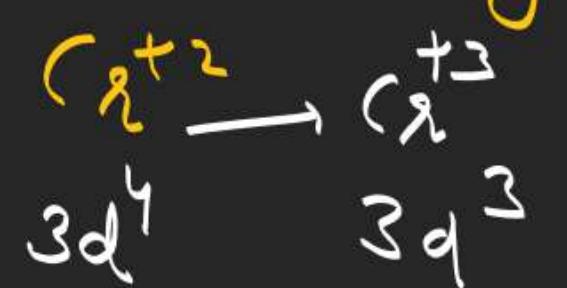
' the metal carbonyl  
Complex compound.



Ques +8 O.S state found in?



Ques  $\text{Cr}^{+2}$  and  $\text{Fe}^{+2}$  which is better reducing agent.





$\text{Cr}^{+2}$  is better

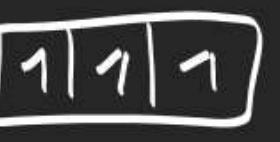
Reducing agent  $\text{Fe}^{+2}$

$\text{Cr}^{+2}$  so it can  
can reduce  $\text{H}^+$   
from dil acid



Imp.

$d^5 > d^3$  [In gaseous]



$d^3 > d^5$  [Magnetic]  
So 1.



## d -BLOCK

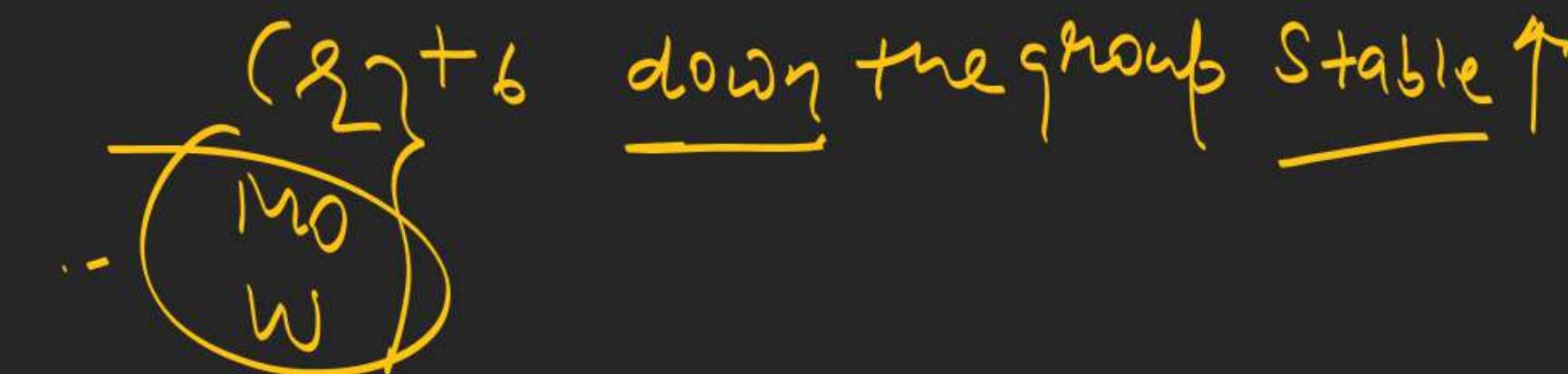
- (5) **The maximum oxidation states of reasonable stability correspond in value to the sum of the s and d electrons upto manganese ( $\text{Ti}^{\text{IV}}\text{O}_2$ ,  $\text{V}^{\text{V}}\text{O}_2^+$ ,  $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ ,  $\text{Mn}^{\text{VII}}\text{O}_4^-$ ) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are  $\text{Fe}^{\text{II,III}}$ ,  $\text{Co}^{\text{II,III}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Cu}^{\text{I,II}}$ ,  $\text{Zn}^{\text{II}}$ .**
- (6) **The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of d orbitals in such a way that their oxidation states differ from each other by unity, e.g.,  $\text{V}^{\text{II}}$ ,  $\text{V}^{\text{III}}$ ,  $\text{V}^{\text{IV}}$ ,  $\text{V}^{\text{V}}$ .**
- (7) **This is in contrast with the variability of oxidation states of non transition elements where oxidation states normally differ by a unit of two.**
- (8) An interesting feature in the variability of oxidation states of the d-block elements is noticed among the groups (groups 4 through 10 ).

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(9) In group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO<sub>3</sub> and WO<sub>3</sub> are not.

(10) Low oxidation states are found when a complex compound has ligands capable of π-acceptor character in addition to the σ-bonding. For example, in Ni(CO)<sub>4</sub> and Fe(CO)<sub>5</sub>, the oxidation state of nickel and iron is zero.

(11) As the oxidation number of a metal increases, ionic character decreases. In the case of Mn, Mn<sub>2</sub>O<sub>7</sub> is a covalent green oil. Even CrO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> have low melting points. In these higher oxides, the acidic character is predominant. Thus,



## d -BLOCK

$\text{Mn}_2\text{O}_7$  gives  $\text{HMnO}_4$  and  $\text{Cr}_2\text{O}_3$  gives  $\text{H}_2\text{CrO}_4$  and  $\text{H}_2\text{Cr}_2\text{O}_7$ .  $\text{V}_2\text{O}_5$  is, however, amphoteric

though mainly acidic and it gives  $\text{VO}_4^{3-}$  as well as  $\text{VO}^{2+}$  salts. In vanadium there is gradual change from the basic  $\text{V}_2\text{O}_3$  to less basic  $\text{V}_2\text{O}_4$  and to amphoteric  $\text{V}_2\text{O}_5$ .  $\text{V}_2\text{O}_4$  dissolves in acids to give  $\text{VO}^{2+}$  salts. Similarly,  $\text{V}_2\text{O}_5$  reacts with alkalies as well as acids to give  $\text{VO}_4^{3-}$  and  $\text{VO}_4^{2-}$  respectively. The well characterised  $\text{CrO}$  is basic but  $\text{Cr}_2\text{O}_3$  is amphoteric.

PYQS

Oxidation state of the 1<sup>st</sup> transition series Most common ones are in bole types:

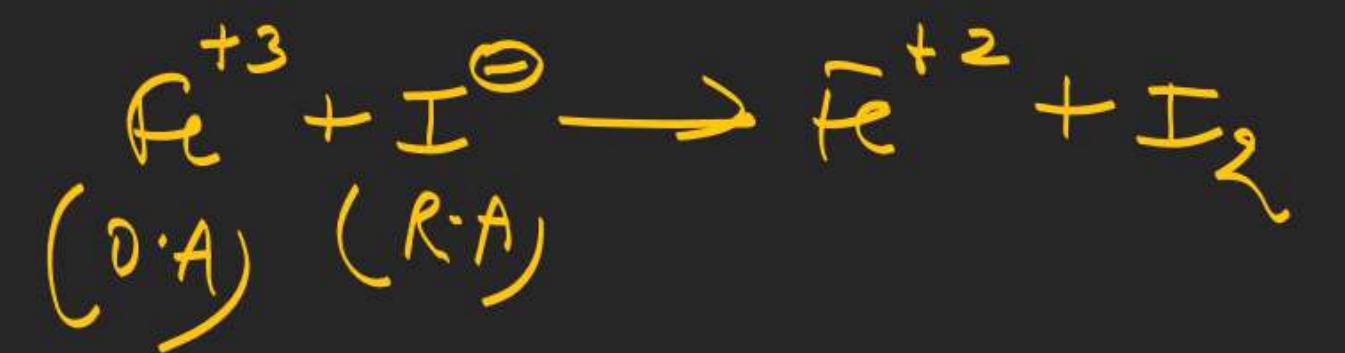
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			+1					+1	
+2	+2	+2	+2	+2	+2	+2	+2	+2	
+3	+3	+3	+3	+3	+3	+3	+3		
+4	+4	+4	+4	+4	+4	+4	+4		
+5	+5	+5	+5						
		+6	+6	+6					
			+7						

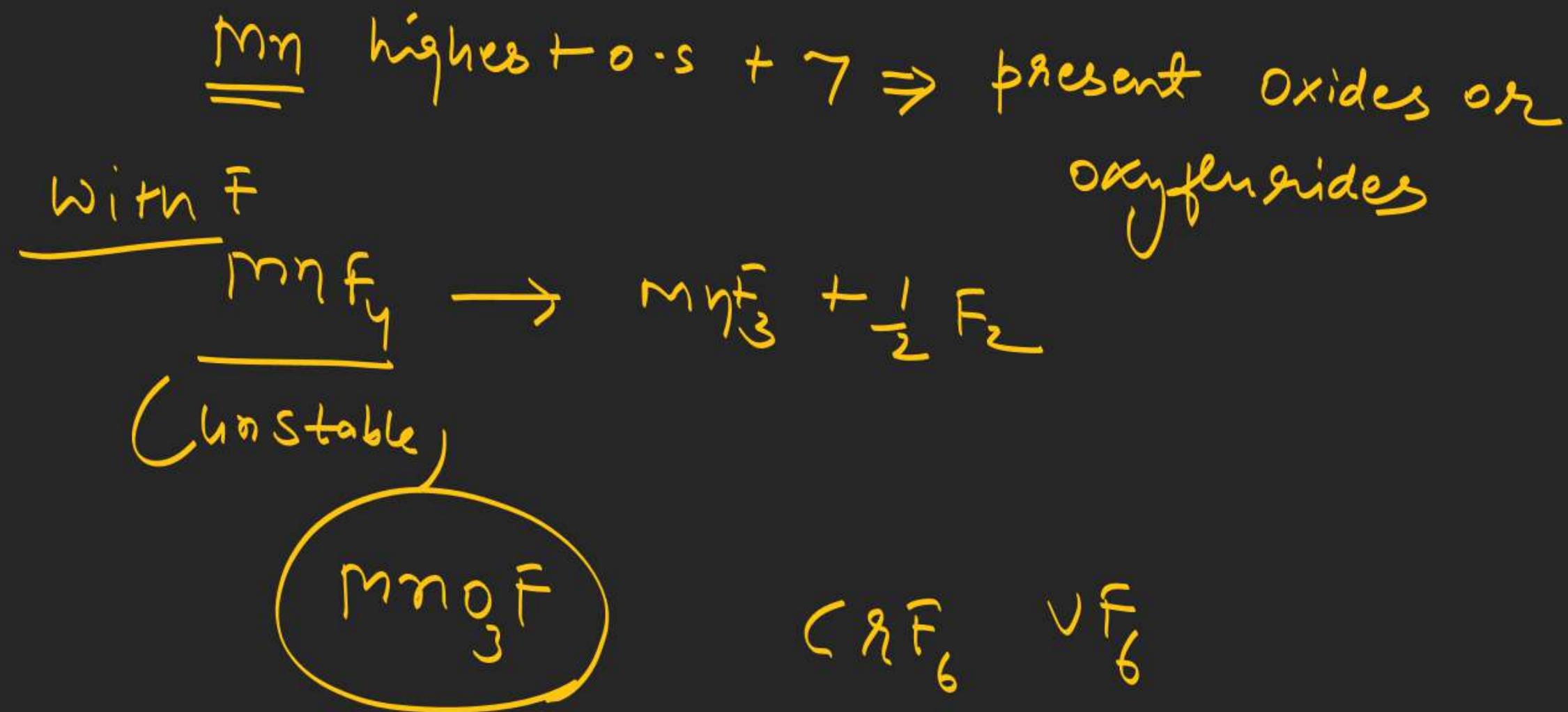


**Trends in stability of higher oxidation state:**

- (1) Table shows the stable halides of the 3 d series of transition metals. The highest oxidation numbers are achieved in  $\text{TiX}_4$  (tetrahalides),  $\text{VF}_5$  and  $\text{CrF}_6$ . The +7 state for Mn is not represented in simple halides but  $\text{MnO}_3\text{F}$  is known, and beyond Mn no metal has a trihalide except  $\text{FeX}_3$  and  $\text{CoF}_3$ .
- (2) The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of  $\text{CoF}_3$ , or higher bond enthalpy terms for the higher covalent compounds, e.g.,  $\text{VF}_5$  and  $\text{CrF}_6$ .
- (3) Although  $\text{V}^{\text{V}}$  is represented only by  $\text{VF}_5$ , the other halides, however, undergo hydrolysis to give oxohalides,  $\text{VOX}_3$ .
- (4) Another feature of fluorides is their instability in the low oxidation states e.g.,  $\text{VX}_2$  ( $\text{X} = \text{Cl, Br or I}$ )

Fe I<sub>3</sub> does not exist



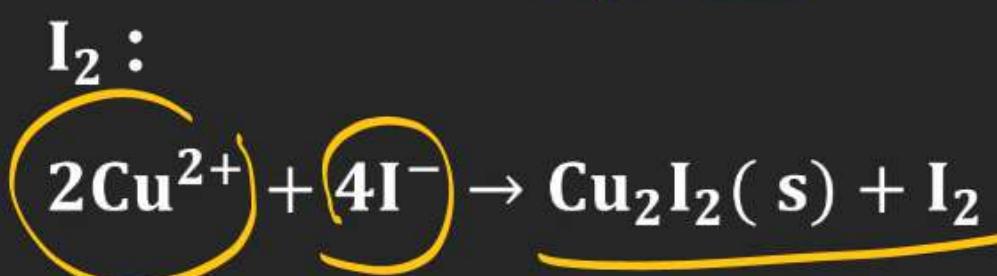


## d -BLOCK

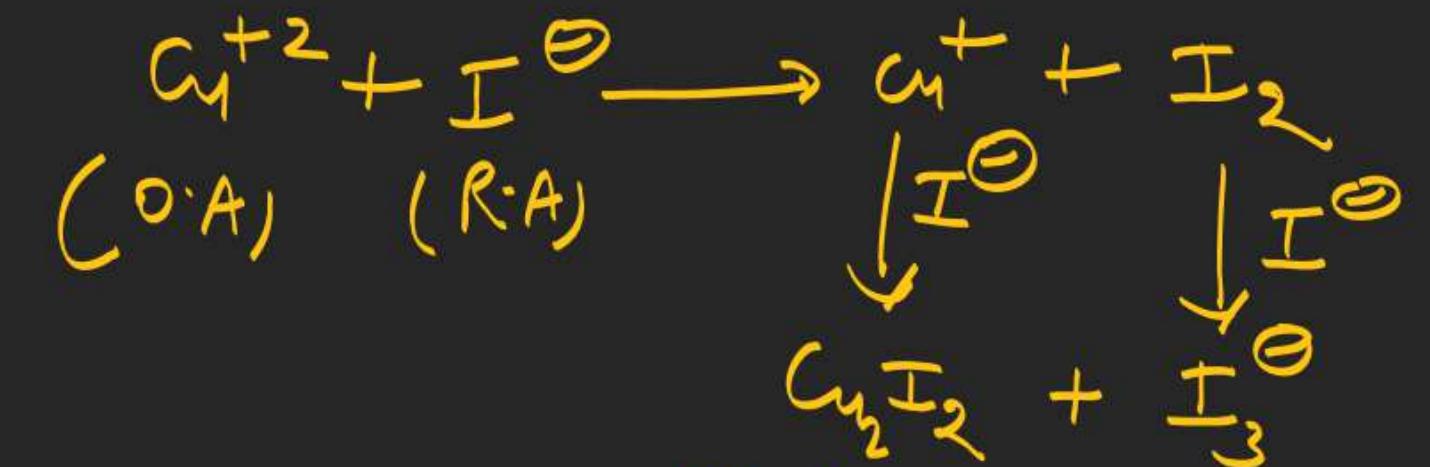
## Formulas of halides of 3d-metals

	Oxidation Number							
+6			CrF <sub>6</sub>					
+5		VF <sub>5</sub>	CrF <sub>5</sub>					
+4	TiX <sub>4</sub>	VX <sub>4</sub> <sup>I</sup>	CrF <sub>4</sub>	MnF <sub>4</sub>				
+3	TiX <sub>3</sub> <sup>III</sup>	VX <sub>3</sub>	CrF <sub>3</sub>	MnF <sub>3</sub>	FeX <sub>3</sub> <sup>I</sup>	CoF <sub>3</sub>	CuX <sub>2</sub> <sup>II</sup>	ZnX <sub>2</sub>
+2	TiX <sub>2</sub>	VX <sub>2</sub>	CrF <sub>2</sub>	MnX <sub>2</sub>	FeX <sub>2</sub>	CoX	NiX <sub>2</sub>	CuX <sup>III</sup>
+1								

**Key : X = F → I; X<sup>I</sup> = F → Br; X<sup>II</sup> = F → Cl; X<sup>III</sup> = Cl → I and the same applies to CuX. On the other hand, all Cu(II) halides are known except the iodide. In this case, Cu<sup>2+</sup> oxidises I<sup>-</sup> to I<sub>2</sub>:**



PyQR CuI<sub>2</sub> does not exist



White ppt + Brown sol

Iodometry test



## d -BLOCK

- (5) However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.
- $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$
- $\text{Cu}^+ < \text{Cu}^{+2}$
- (6) The stability of  $\text{Cu}^{2+}$  (aq) rather than  $\text{Cu}^+$  (aq) is due to the much more negative  $\Delta_{\text{Hyd}}H^\Theta$  of  $\text{Cu}^{2+}$  (aq) than  $\text{Cu}^+$ , which more than compensates for the second ionisation enthalpy of Cu.
- (7) The ability of oxygen to stabilise the highest oxidation state is demonstrated in the oxides.
- (8) The highest oxidation number in the oxides coincides with the group number and is attained in  $\text{Sc}_2\text{O}_3$  to  $\text{Mn}_2\text{O}_7$ .

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- (9) Beyond Group 7, no higher oxides of Fe above  $\text{Fe}_2\text{O}_3$ , are known, although ferrates (VI)  $(\text{FeO}_4)^{2-}$ , are formed in alkaline media but they readily decompose to  $\text{Fe}_2\text{O}_3$  and  $\text{O}_2$ .
- $$\text{Fe}^{+2} \rightleftharpoons \text{Fe}^{+3}$$
- (10) Besides the oxides, oxocations stabilise V<sup>V</sup> as  $\text{VO}_2^+$ , V<sup>IV</sup> as  $\text{VO}^{2+}$  and Ti<sup>IV</sup> as  $\text{TiO}^{2+}$
- (11) The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. Thus the highest Mn fluoride is  $\text{MnF}_4$  whereas the highest oxide is  $\text{Mn}_2\text{O}_7$ . The ability of oxygen to form multiple bonds to metals explains its superiority.
- (12) In the covalent oxide  $\text{Mn}_2\text{O}_7$ , each Mn is tetrahedrally surrounded by O's including a Mn-O-Mn bridge.
- (13) The tetrahedral  $[\text{MO}_4]^n$  ions are known for V<sup>V</sup>, Cr<sup>VI</sup>, Mn<sup>V</sup>, Mn<sup>VI</sup> and Mn<sup>VII</sup>.

FORMATION OF



**COLOURED ION:****Colour: (aquated)** $\text{Ta}^{4+} \rightarrow \text{colourless}$  $\text{V}^{4+} \rightarrow \text{blue}$  $\text{V}^{2+} \rightarrow \text{violet}$  $\text{Cr}^{3+} \rightarrow \text{green}$  $\text{Mn}^{2+} \rightarrow \text{light pink}$  $\text{Fe}^{3+} \rightarrow \text{yellow}$  $\text{Ni}^{2+} \rightarrow \text{green}$  $\text{Zn}^{2+} \rightarrow \text{colourless}$  $\text{Sc}^{3+} \rightarrow \text{colourless}$  $\text{Ti}^{3+} \rightarrow \text{purple}$  $\text{V}^{3+} \rightarrow \text{green}$  $\text{Cr}^{2+} \rightarrow \text{blue}$  $\text{Mn}^{3+} \rightarrow \text{violet}$  $\text{Fe}^{2+} \rightarrow \text{light green}$  $\text{Co}^{2+} \rightarrow \text{pink}$  $\text{Cu}^{2+} \rightarrow \text{blue}$

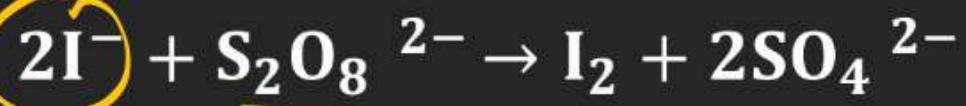
## CATALYTIC PROPERTIES

- (1) **The transition metals and their compounds are known for their catalytic activity.**  
**This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in Catalytic Hydrogenation) are some of the examples.**
- (2) **Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3d and 4 s electrons for bonding).**
- (3) **This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering).**

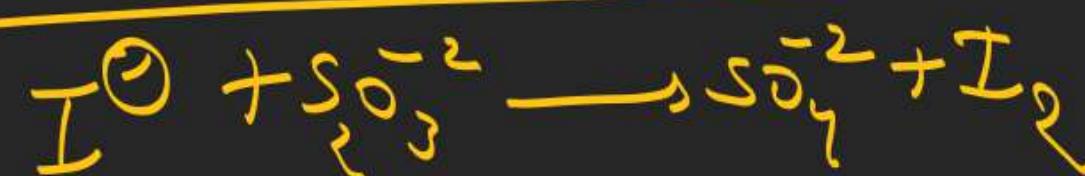
$$\Sigma_2^{08} + I^{\ominus} \longrightarrow x$$

## d -BLOCK

- (4) Also because the transition metal ions can change their oxidation states, they become more effective as catalysts. For example, iron(III) catalyses the reaction between iodide and persulphate ions.



An explanation of this catalytic action can be given as:



## d -BLOCK

*active species*

Catalyst	$TiCl_4 + Al(C_2H_5)_3$	Used
$TiCl_3 \rightarrow$	Used as the Ziegler-Natta catalyst in the production of polythene.	
$V_2O_5 \rightarrow$	Convert $SO_2$ to $SO_3$ in the contact process for making $H_2SO_4$	
$MnO_2 \rightarrow$	Used as a catalyst to decompose $KClO_3$ to give $O_2$ $KClO_3 \xrightarrow{\Delta} KCl + O_2$	
$Fe \rightarrow$	Promoted iron is used in the Haber-Bosch process for making $NH_3$	
$FeCl_3 \rightarrow$	Used in the production of $CCl_4$ from $CS_2$ and $Cl_2$	
$\star PdCl_2 \rightarrow$	Wacker process for converting $C_2H_4 + H_2O + PdCl_2$ to $CH_3CHO + 2HCl + Pd$ .	
$Pd \rightarrow$	Used for hydrogenation (e.g. phenol to cyclohexanone).	
$Pt/PtO \rightarrow$	Adams catalyst, used for reductions.	
$Pt \rightarrow$	Formerly used for $SO_2 \rightarrow SO_3$ in the contact process for making $H_2SO_4$	
$\star Pt/Rh \rightarrow$	Formerly used in the Ostwald process for making $HNO_3$ to oxidize $NH_3$ to $NO$	
$Cu \rightarrow$	Is used in the direct process for manufacture of $(CH_3)_2SiCl_2$ used to make silicones.	

# d -BLOCK

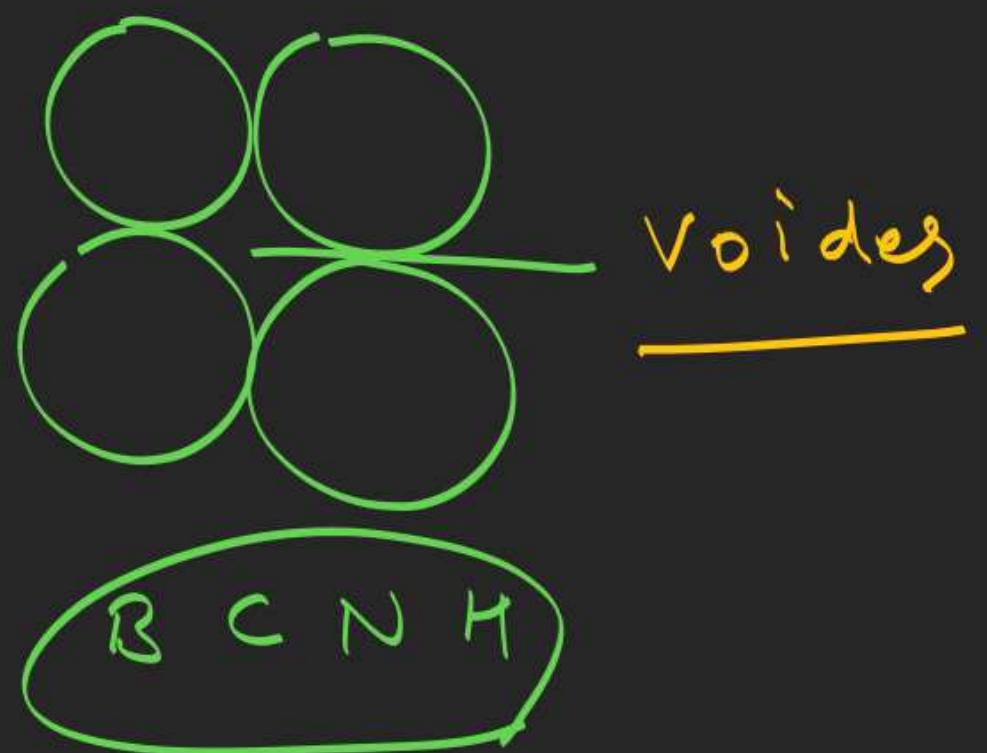
Cu/V →	Oxidation of cyclohexanol/cyclohexanone mixture to adipic acid which is used to make nylone- 66
 CuCl <sub>2</sub> →	Decon process of making Cl <sub>2</sub> from HCl
Ni →	Raney nickel, numerous reduction processes (e.g. manufacture of hexamethylenediamine, production of H <sub>2</sub> from NH <sub>3</sub> , reducing anthraquinone to anthraquinol in the production of H <sub>2</sub> O <sub>2</sub> )

## Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. The principal physical and chemical characteristics of these compounds are as follows:

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

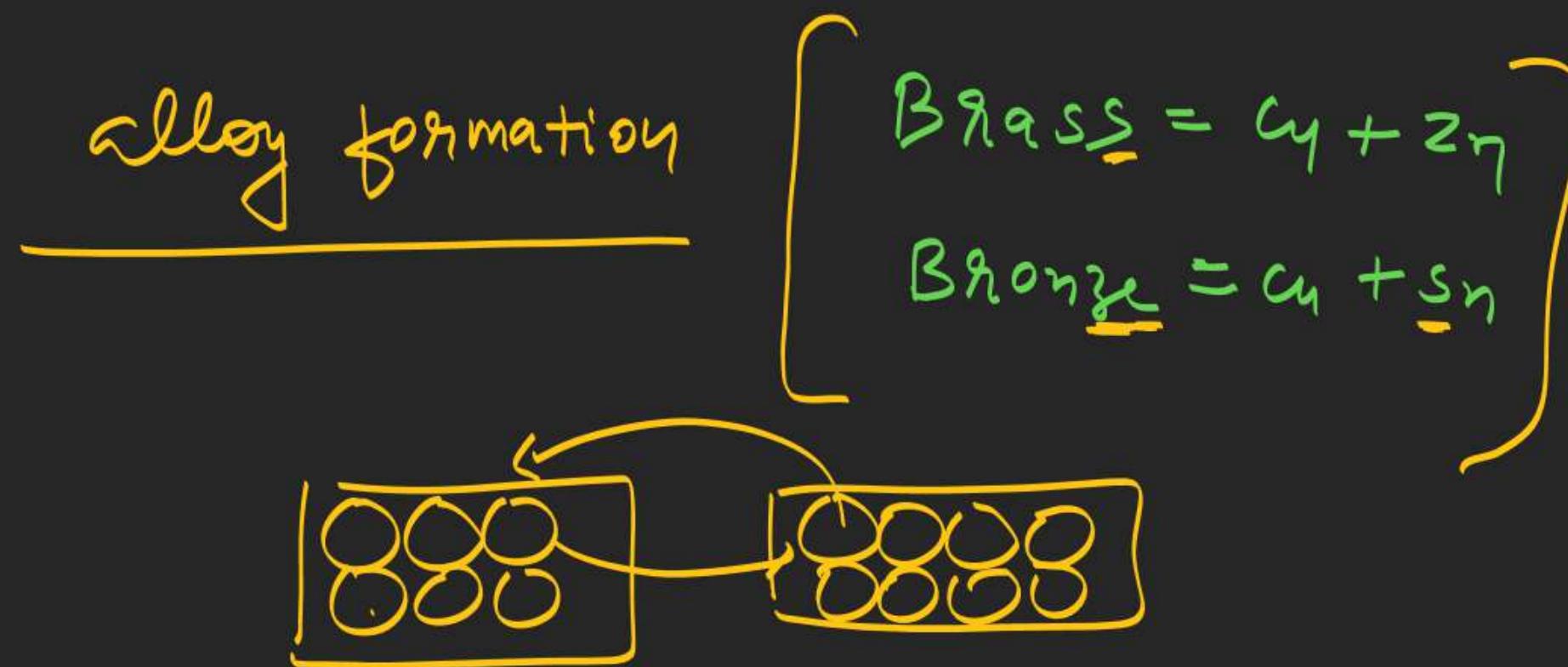
## Interstitial compound



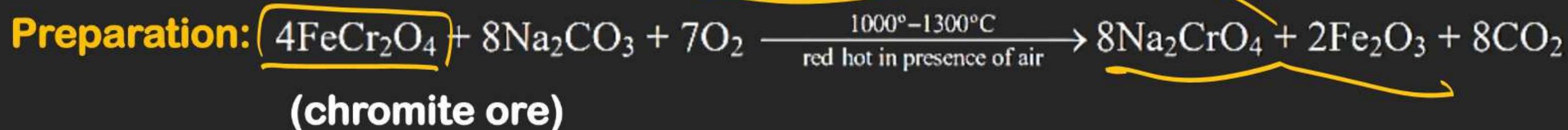
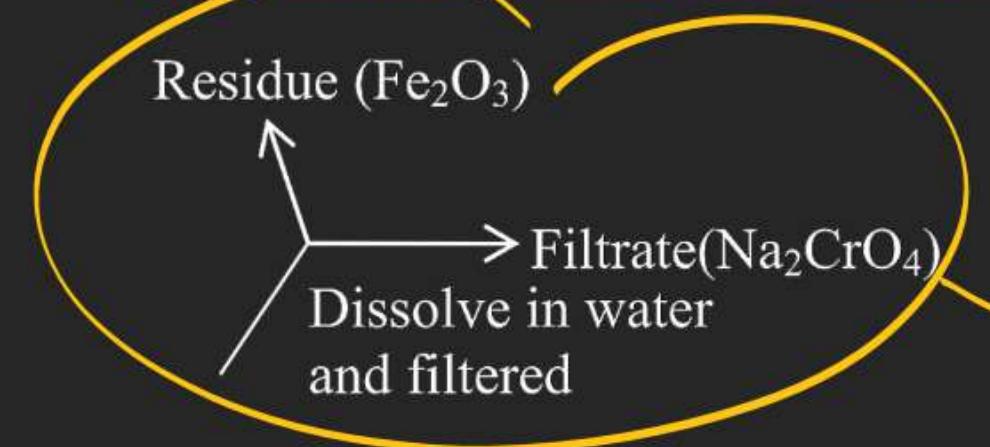
## Alloy Formation

An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other.

Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel. Alloys of transition metals with non transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance.



Hg can form alloy with many metals  
except  $\text{Fe}$   $\text{Pt}$   $\text{W}$

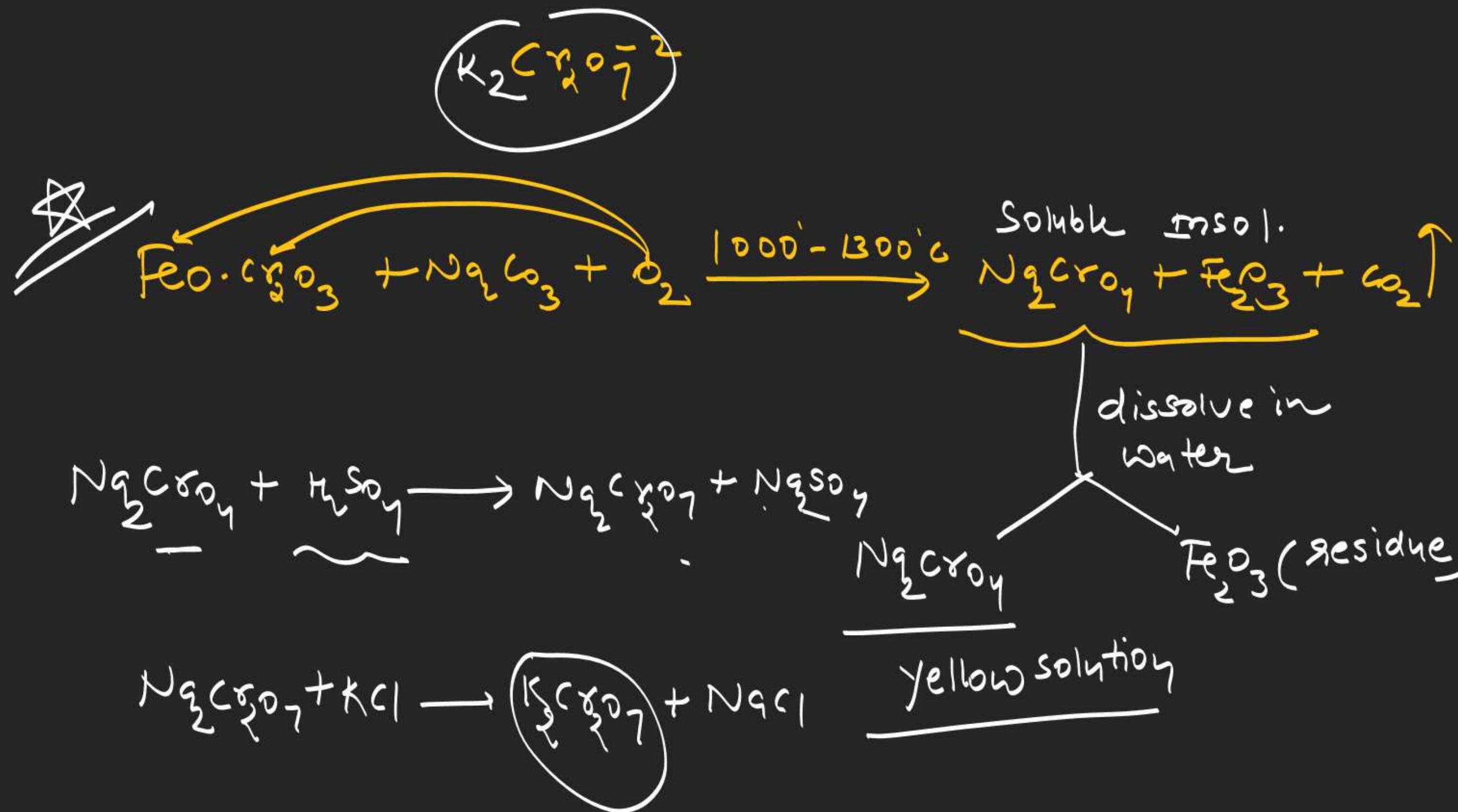
**d -BLOCK****CHROMATE – DICHROMATE**

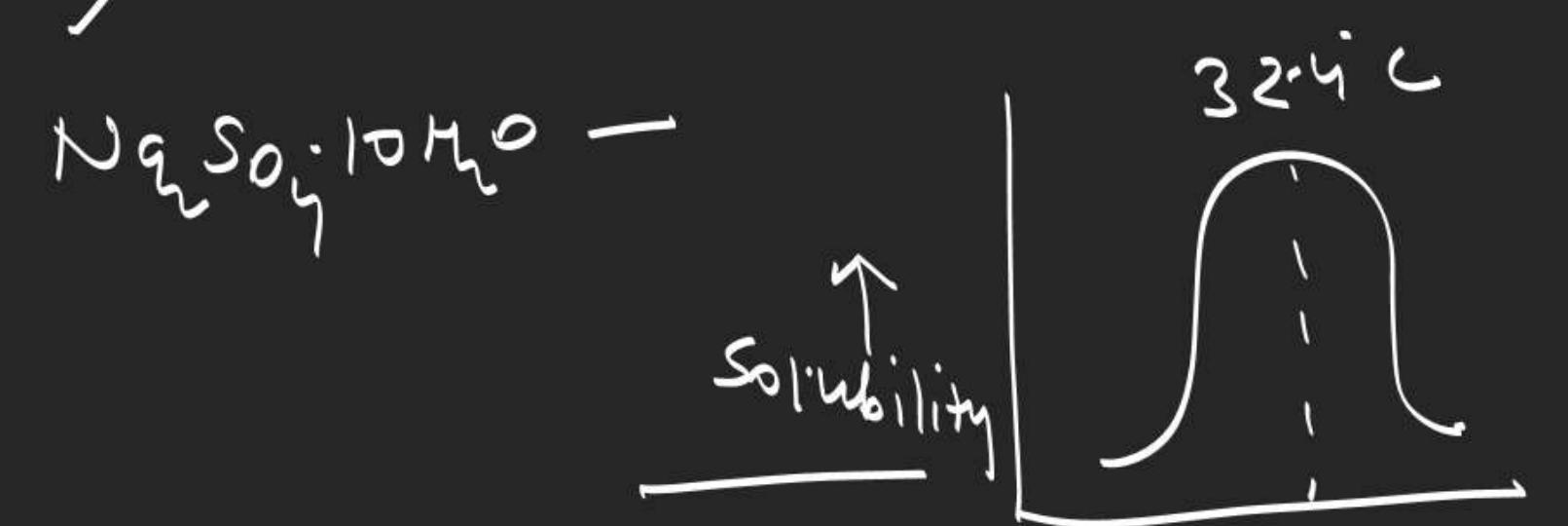
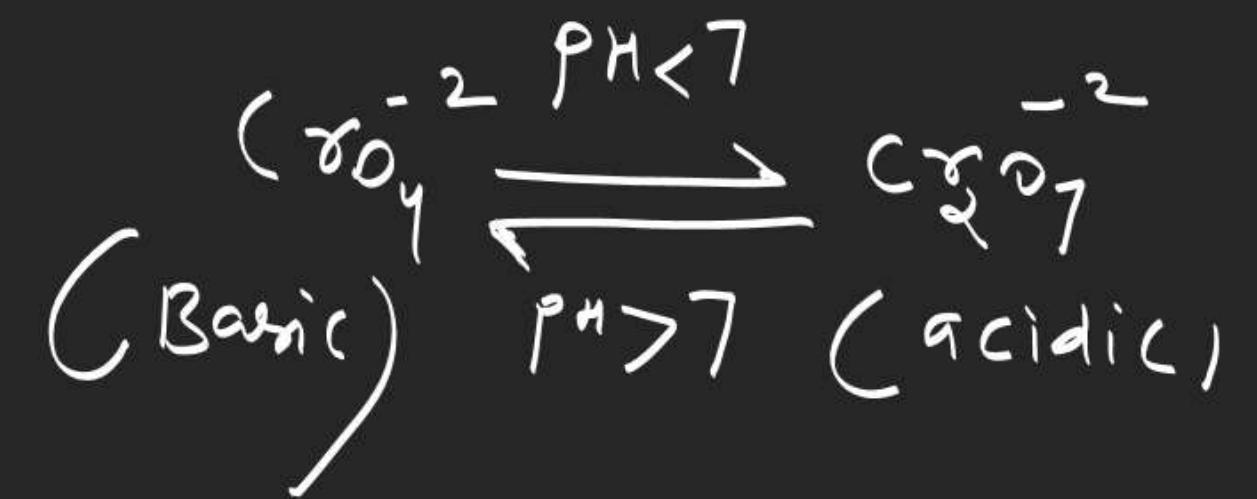
[Lime ( $\text{CaO}$ ) added with  $\text{Na}_2\text{CO}_3$  which keeps the mass porous so that air has access to all parts and prevents fusion]



Its solubility  
Conc. upto  $32^\circ\text{C}$  increases  
And then decreases

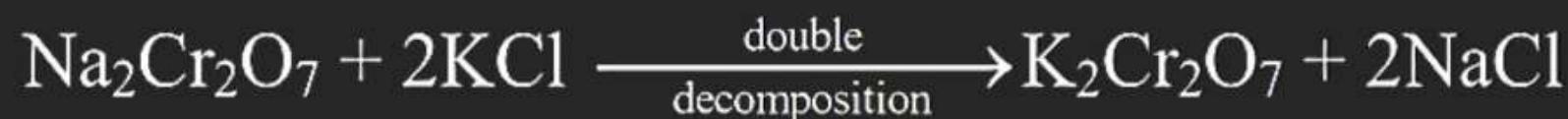
Hence, suitable temp. is to be employed to crystallise out  $\text{Na}_2\text{SO}_4$  first.





Then  $\text{Na}_2\text{Cr}_2\text{O}_7$  is crystallised out as  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  on evaporation.  
(red crystal)

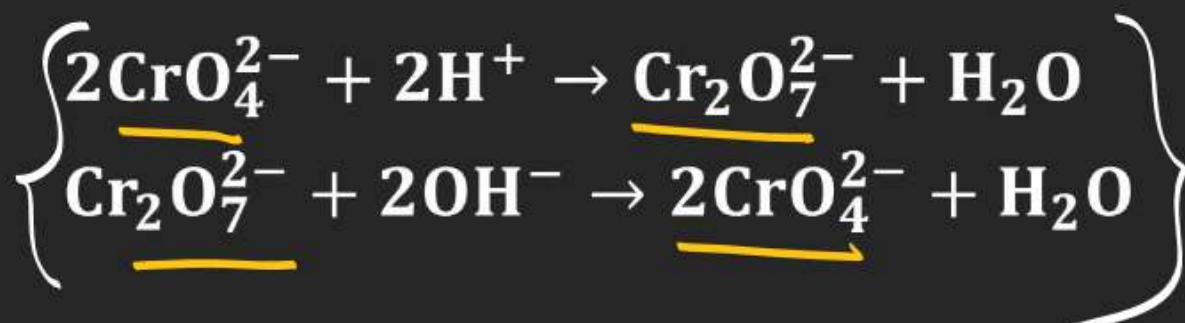
**How to get  $\text{K}_2\text{Cr}_2\text{O}_7$  :**



**Hot conc.**

$\text{NaCl}$  crystallises out first and filtered off. Then  $\text{K}_2\text{Cr}_2\text{O}_7$  crystallised out on cooling

The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

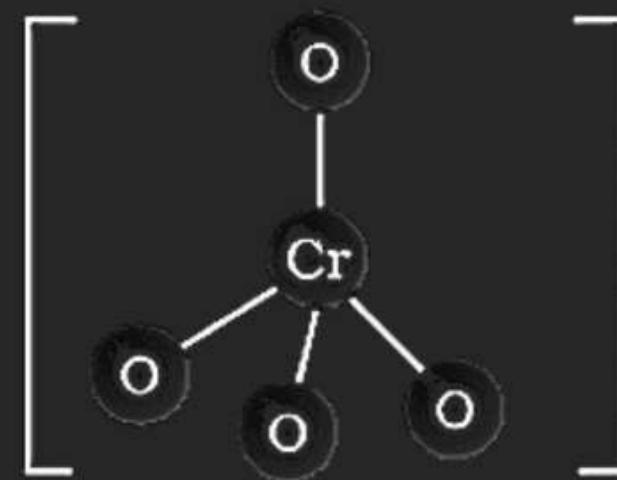


## d -BLOCK

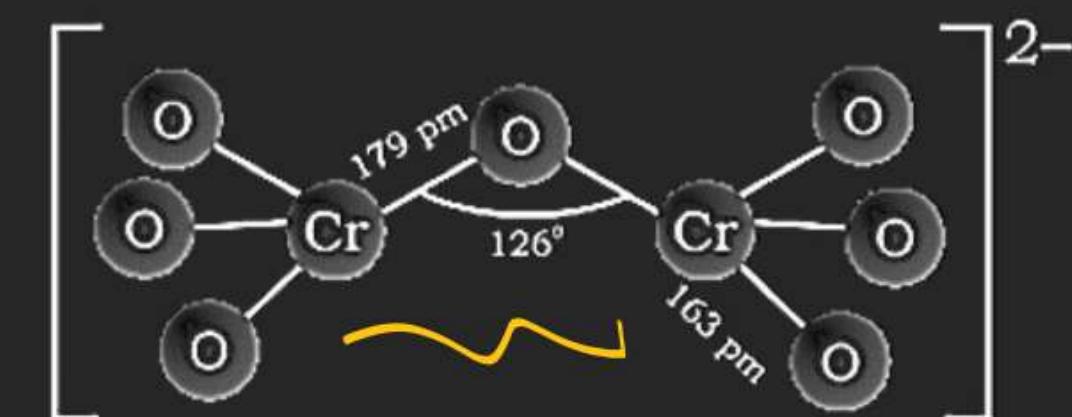
The structures of chromate ion,  $\text{CrO}_4^{2-}$  and the dichromate ion,  $\text{Cr}_2\text{O}_7^{2-}$  are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with  $\text{Cr} - \text{O} - \text{Cr}$  bond angle of  $126^\circ$ . Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry.



Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action can be represented as follows:

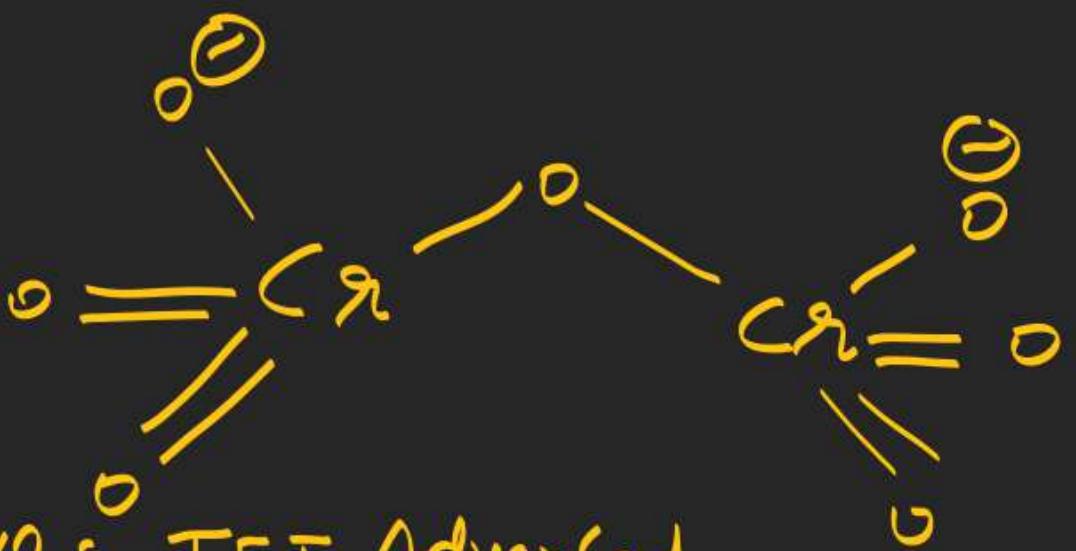
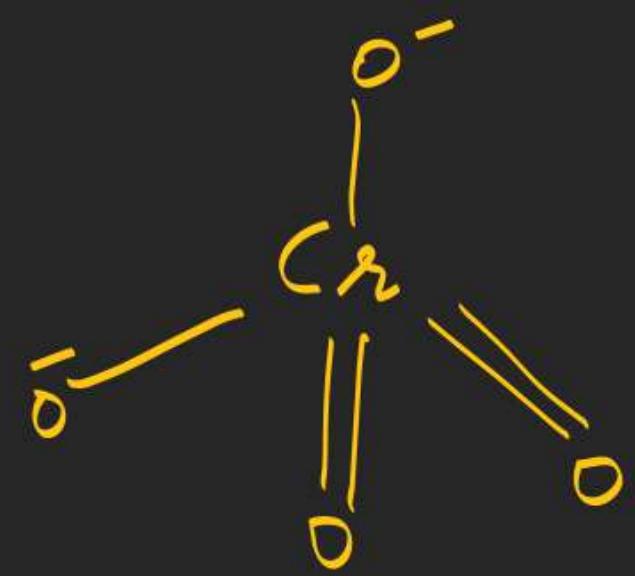


Chromate ion



Dichromate ion

Ques  $\text{Na}_2\text{CrO}_7$  is not used as primary standard Why

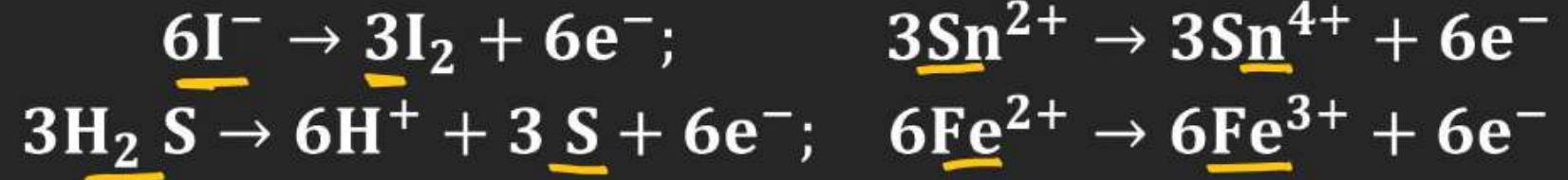


PYQS JEE Advanced  
Two Identical Cr-O bonds

(K)

## d -BLOCK

Thus, acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin (II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:



The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, for e.g.,

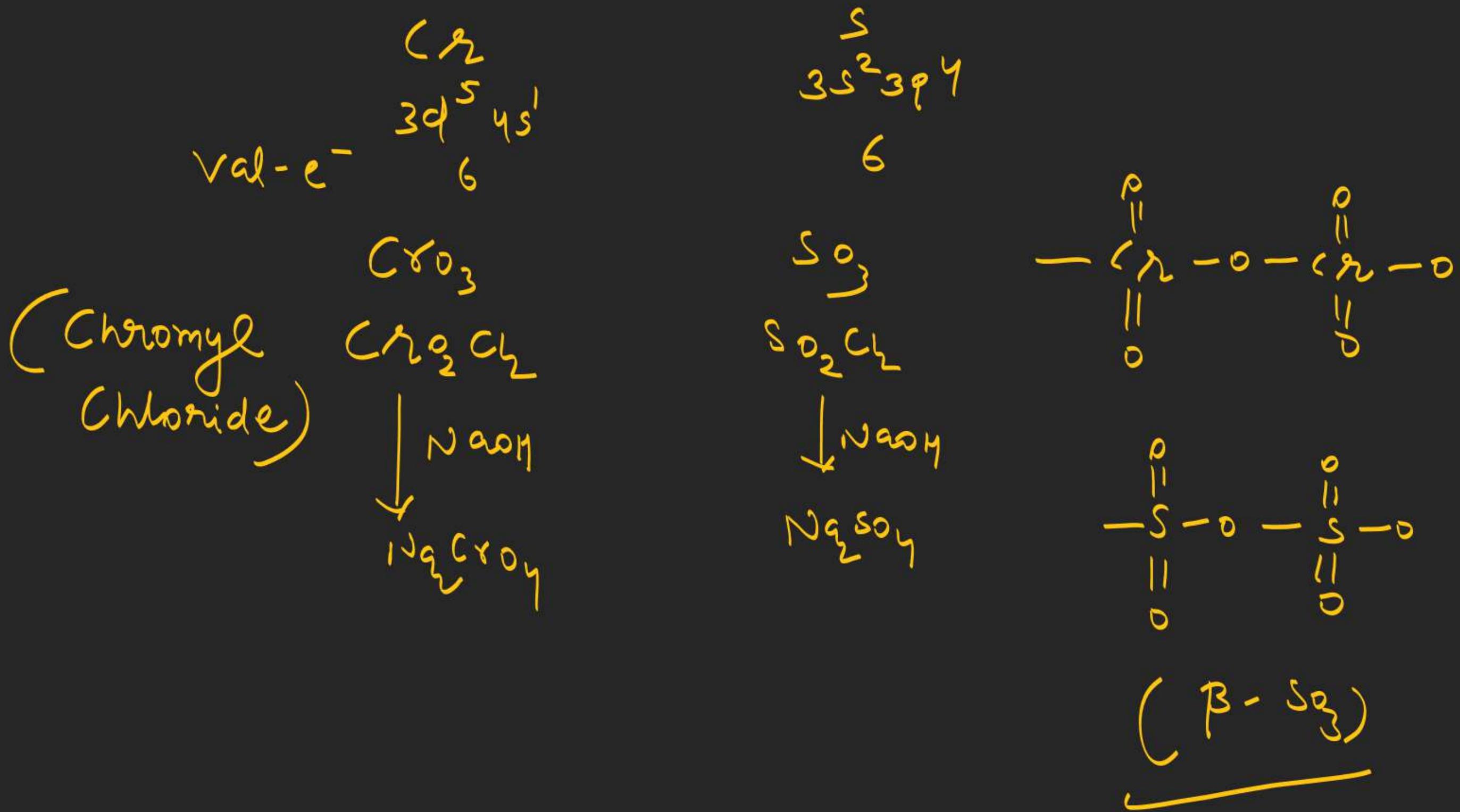


Similarities between hexavalent Cr & S-compounds:

(i)  $\text{SO}_3$  &  $\text{CrO}_3$  → both acidic.

(ii)  $\text{S} \rightarrow \text{SO}_4^{2-}, \text{S}_2\text{O}_7^{2-}$ ,  $\text{Cr} \rightarrow \text{CrO}_4^{2-}, \text{Cr}_2\text{O}_7^{2-}$

(iii)  $\text{CrO}_4^{-2}$  &  $\text{SO}_4^{2-}$  are isomorphous



$MnO_4^-$  $C_2O_4^{2-}$ 

$$Mn^{+3} / Mn^{+2} = 1.51$$

$$C_2^{+3} / C_2^{+2} = -0.41$$

$$\Delta G = -\gamma F E^\circ$$

$$\Delta G = -\gamma F E^\circ$$

$$C_2^{+3} > C_2^{+2}$$

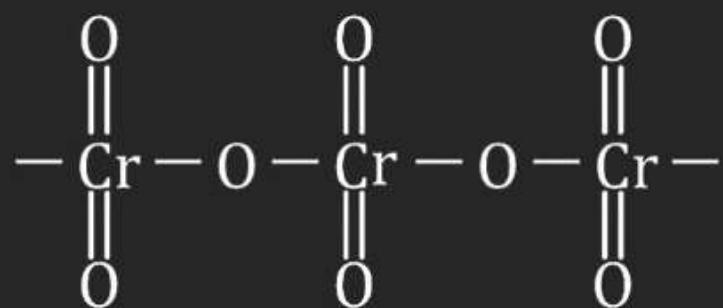
$\star$   $Mn^{+2} > Mn^{+3}$

## d -BLOCK

(iv)  $\text{SO}_2\text{Cl}_2 \& \text{CrO}_2\text{Cl}_2 \xrightarrow{\text{OH}^-} \text{SO}_4^{2-} \& \text{CrO}_4^{2-}$  respectively.

(v)  $\text{SO}_3\text{Cl}^- \& \text{CrO}_3\text{Cl}^- \xrightarrow{\text{OH}^-} \text{SO}_4^{2-} \& \text{CrO}_4^{2-}$

(vi)  $\text{CrO}_3$  &  $\beta(\text{SO}_3)$  has same structure

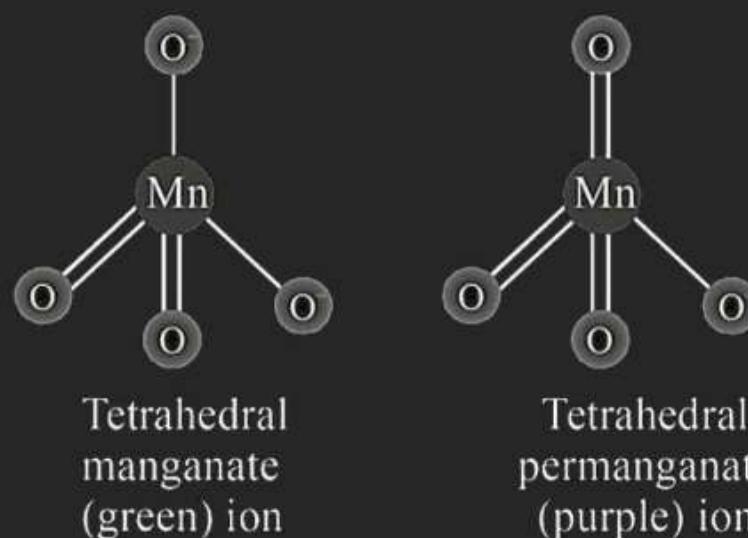
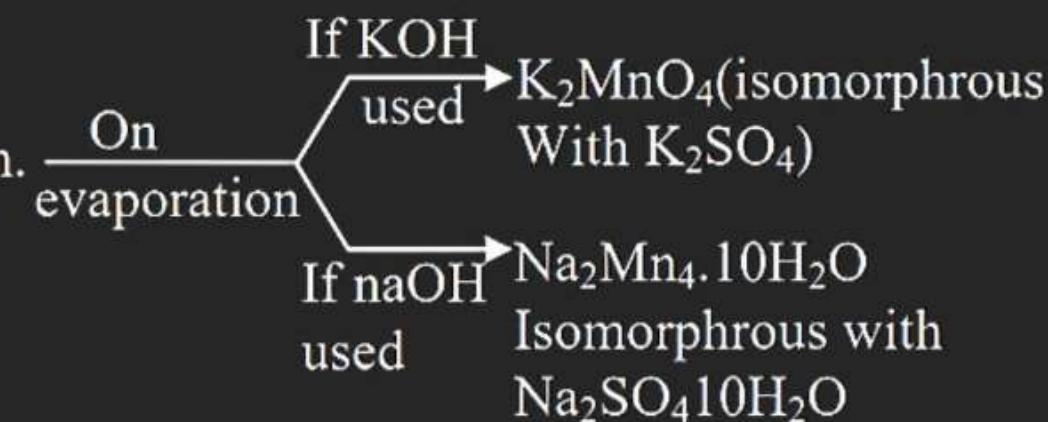


Q. In laboratory  $\text{K}_2\text{Cr}_2\text{O}_7$  is used mainly not  $\text{Na}_2\text{Cr}_2\text{O}_7$ . Why?

Sol.  $\text{Na}_2\text{Cr}_2\text{O}_7$  is deliquescent enough and changes its concentration and can not be taken as primary standard solution whereas  $\text{K}_2\text{Cr}_2\text{O}_7$  has no water of crystallisation and not deliquescent.

**MANAGANATE & PERMANGANATE****PREPARATION OF MANGANATE ( $\text{MnO}_4^{2-}$ ) :-**

Green melt

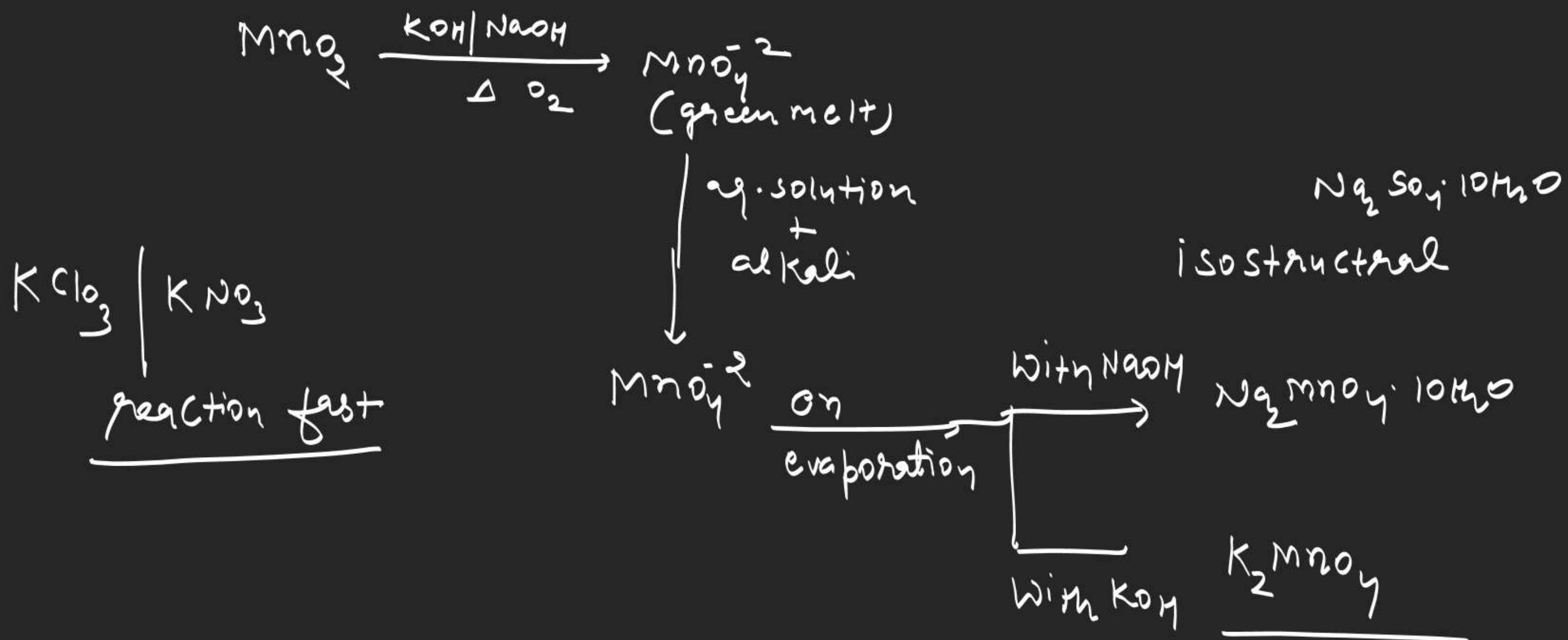
Cold Water  
+ little alkali

MnO<sub>4</sub><sup>-2</sup>  $\Rightarrow$  stable in  
only strong alkaline solution

acidic | light basic | neutral  $\Rightarrow$  disrupt



$$7 - 4 = 3$$



**d -BLOCK**

In presence of  $\text{KClO}_3$  &  $\text{KNO}_3$  the above reaction is more faster because these two on decomposition provides  $\text{O}_2$  easily.

Manganate is also obtained when  $\text{KMnO}_4$  is boiled with KOH.



**Properties:** The above green solution is quite stable in alkali, but in pure water and in presence of acids, depositing  $\text{MnO}_2$  and giving a purple solution of permanganate.



Prove that  $\text{MnO}_4^{2-}$  will disproportionate in acidic medium.

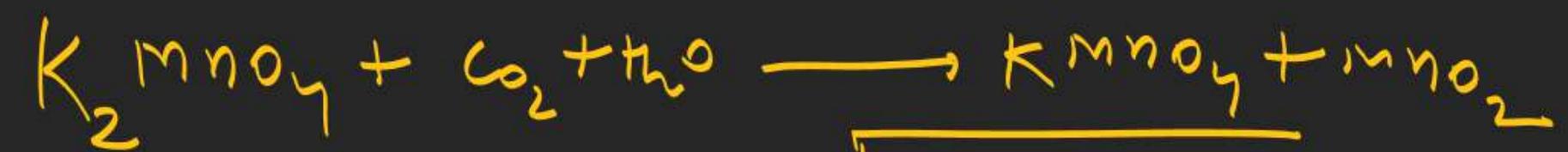
Conversion of  $\text{MnO}_4^{2-}$  to  $\text{MnO}_4^-$



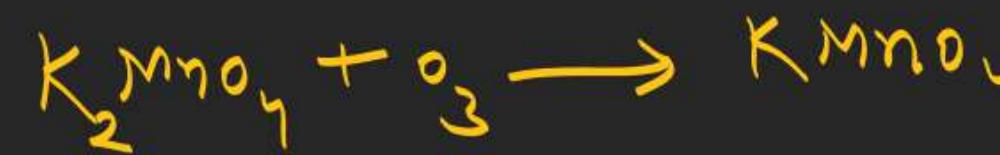
Lab prep of  $K_2MnO_4$



Prep of  $KMnO_4$



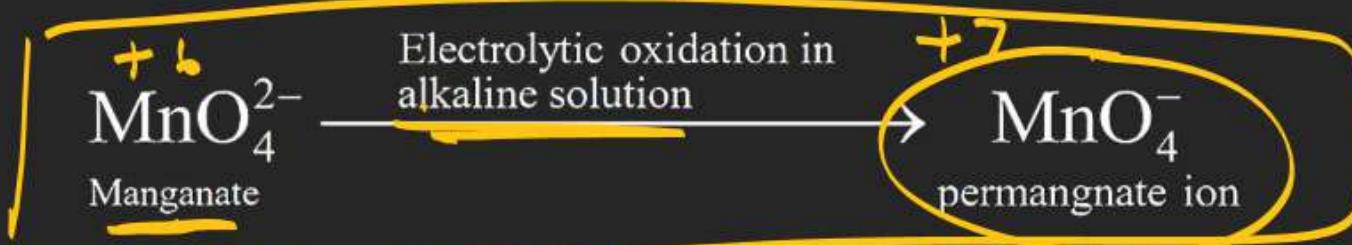
1/3 Mn lose



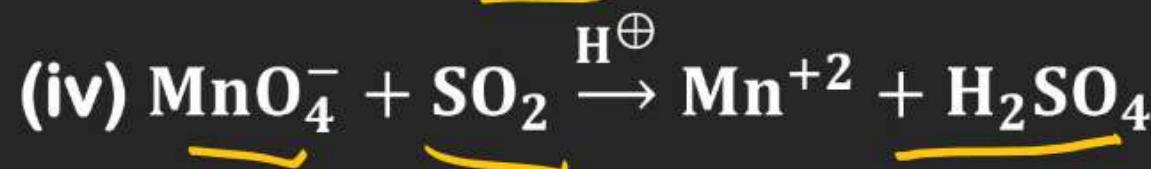
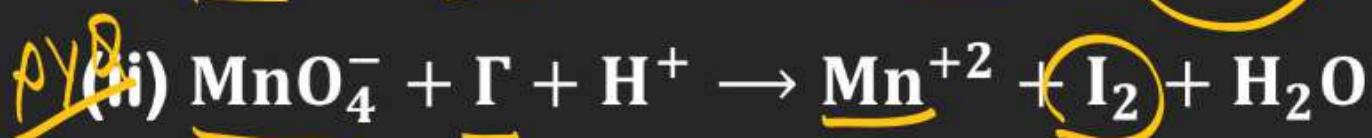
But in the above method  $\frac{1}{3}$  of Mn is lost as  $MnO_2$  but when oxidised either by  $Cl_2$  or by  $O_3$



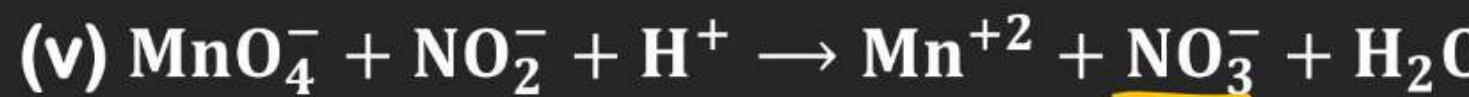
OR



Oxidising Prop. of  $KMnO_4$  : (in acidic medium)



## d -BLOCK



(1) It is not a primary standard since it is difficult to get it in a high degree of purity and free from traces of  $\text{MnO}_2$ .

(2) It is slowly reduced to  $\text{MnO}_2$  especially in presence of light or acid



Hence it should be kept in dark bottles and standardise just before use.



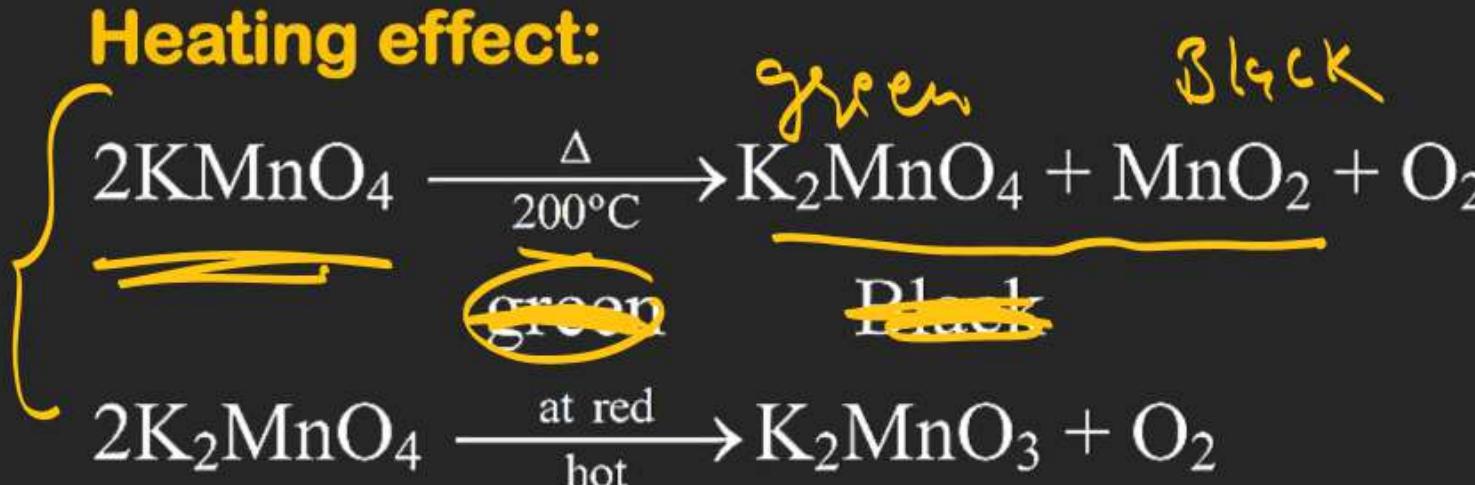
Note: Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.

Oxidising Prop. of  $\text{KMnO}_4$  in neutral or faintly alkaline solution

**Uses of KMnO<sub>4</sub>:**

**Besides its use in analytical chemistry, potassium permanganate is used as a best oxidant in preparative organic chemistry. Its uses for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.**

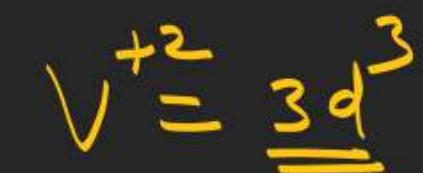
**In laboratory conversion of Mn<sup>+2</sup> to MnO<sub>4</sub><sup>-</sup> is done by :**

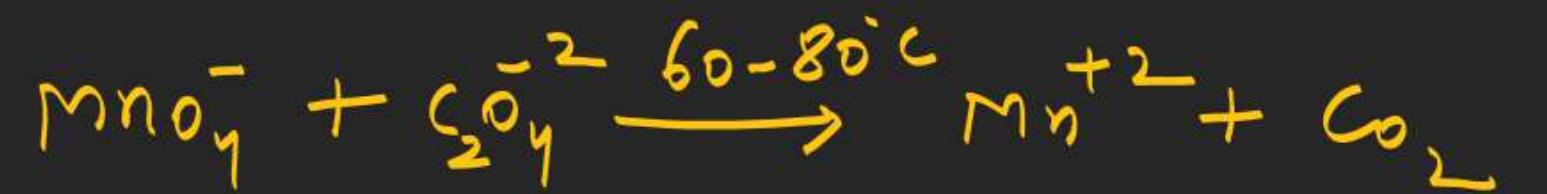
**Heating effect:**

## d -BLOCK

2023

1. The magnetic moment of a transition metal compound has been calculated to be 3.87 B.M. The metal ion is
- (A)  $\text{Cr}^{2+}$       (B)  $\text{Mn}^{2+}$       (C)  $\text{V}^{2+}$       (D)  $\text{Ti}^{2+}$



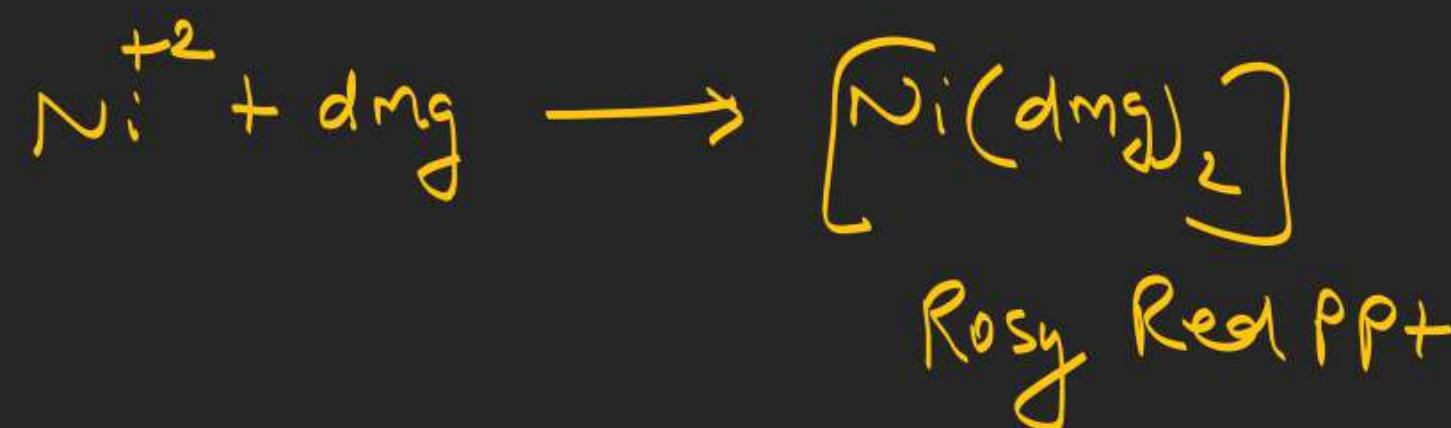


$\text{Mn}^{+2}$  = Auto Catalyst

$\text{MnO}_4^-$  = Sel<sup>k</sup> Indicator

## d -BLOCK

2. An ammoniacal metal salt solution gives a brilliant red precipitate on addition of dimethylglyoxime. The metal ion is :

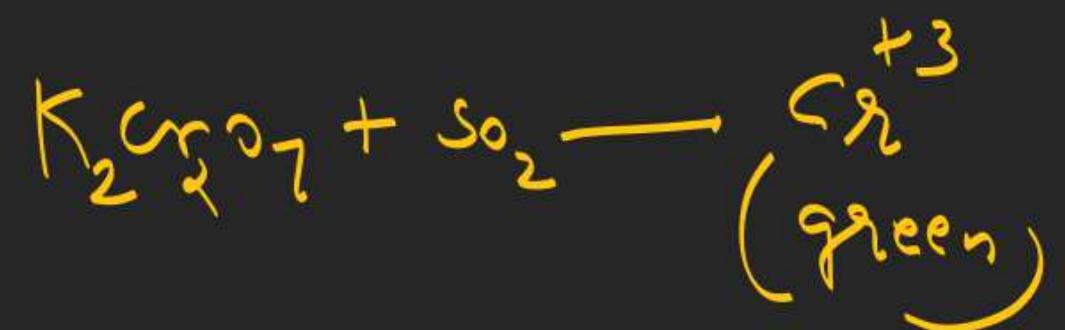
(A)  $\text{Cu}^{2+}$ (B)  $\text{Co}^{2+}$ (C)  $\text{Fe}^{2+}$ (D)  $\text{Ni}^{2+}$ 

**d -BLOCK**

3.  $K_2Cr_2O_7$  paper acidified with dilute  $H_2SO_4$  turns green when exposed to

- (A) Carbon dioxide
- (B) Sulphur trioxide
- (C) Hydrogen sulphide

- (D) Sulphur dioxide



**d -BLOCK**

4. Potassium dichromate acts as a strong oxidizing agent in acidic solution.

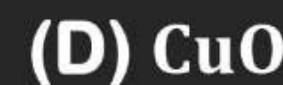
During this process, the oxidation state changes from

- (A) +3 to +1      ~~(B) +6 to +3~~      (C) +2 to +1      (D) +6 to +2



**d -BLOCK**

5. During the borax bead test with  $\text{CuSO}_4$ , a blue green colour of the bead was observed in oxidizing flame due to the formation of



## d -BLOCK

6. The set of correct statements is:

- (i) Manganese exhibits +7 oxidation state in its oxide.
- (ii) Ruthenium and Osmium exhibit +8 oxidation in their oxides.
- (iii) Sc shows ~~+4~~ oxidation state which is oxidizing in nature.
- (iv) Cr shows oxidizing nature in +6 oxidation state.
- (A) (ii) and (iii)
- (B) (i), (ii) and (iv)
- (C) (i) and (iii)
- (D) (ii), (iii) and (iv)

$$S_C = 3d^1 4s^2$$



d -BLOCK

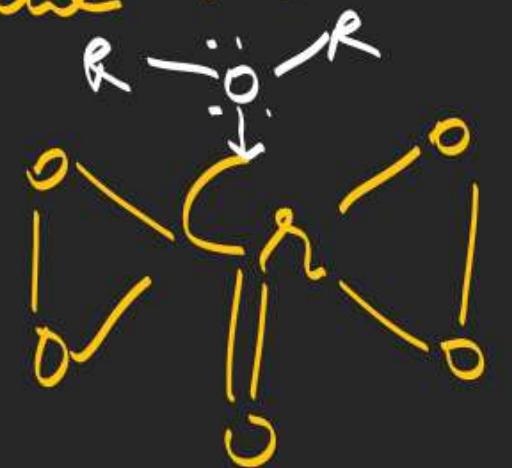
7.

**A solution of CrO<sub>5</sub> in amyl alcohol has a....colour**



$\text{CrO}_5$  is blue a Blue colour

# Compound



two three memb. Rings

Qo it is unstable

and it's blue colour

leads away

but in presence of organic  
it becomes stable

**d -BLOCK**

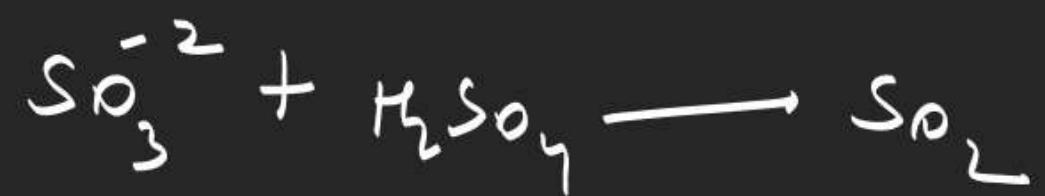
8. During the qualitative analysis of  $\text{SO}_3^{2-}$  using dilute  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_2$  gas is evolved which turns  $\text{K}_2\text{Cr}_2\text{O}_7$  solution (acidified with dilute  $\text{H}_2\text{SO}_4$ ):

(A) Black

(B) Red

(C) Green

(D) Blue



## d -BLOCK

9. When  $\text{Cu}^{2+}$  ion is treated with KI, a white precipitate, X appears in solution. The solution is titrated with sodium thiosulphate, the compound Y is formed. X and Y respectively are

(A)  $\text{X} = \text{Cu}_2\text{I}_2$

~~(B)  $\text{X} = \text{Cu}_2\text{I}_2$~~

(C)  $\text{X} = \text{CuI}_2$

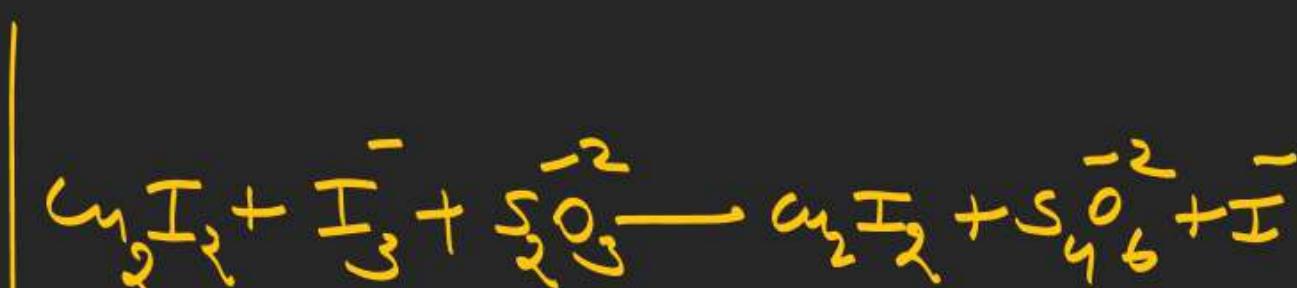
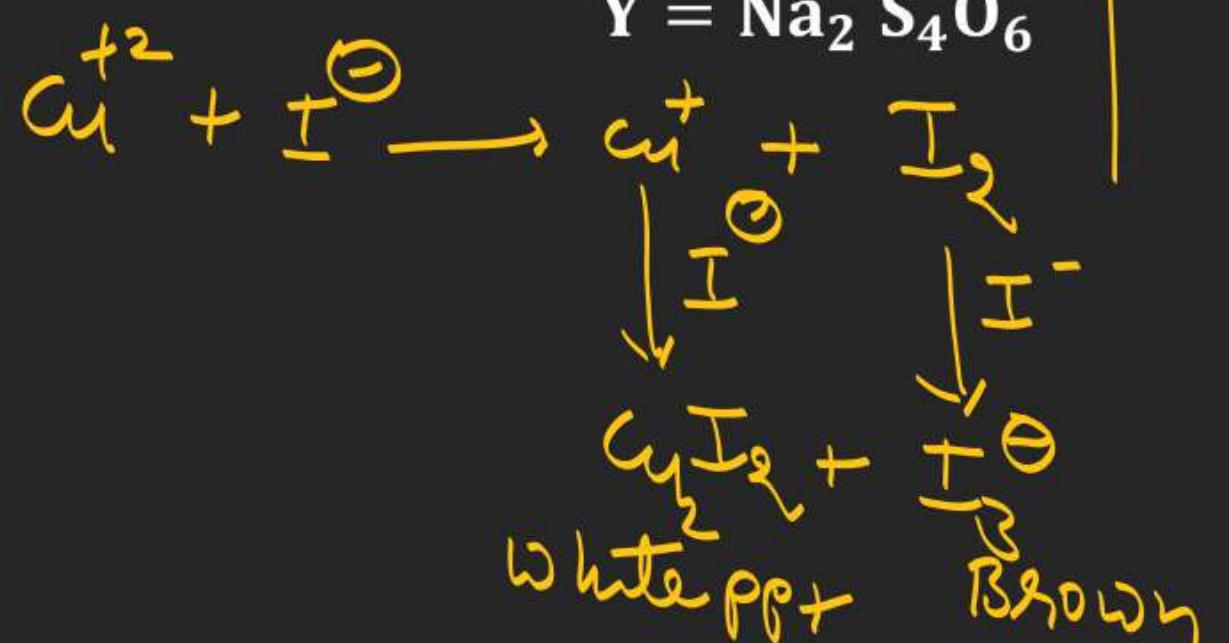
(D)  $\text{X} = \text{CuI}_2$

$\text{Y} = \text{Na}_2\text{S}_4\text{O}_5$

$\text{Y} = \text{Na}_2\text{S}_4\text{O}_6$

$\text{Y} = \text{Na}_2\text{S}_4\text{O}_3$

$\text{Y} = \text{Na}_2\text{S}_4\text{O}_6$



## d -BLOCK

10. The correct order of basicity of oxides of vanadium is

- ~~(A)  $V_2O_3 > V_2O_4 > V_2O_5$~~       (B)  $V_2O_3 > V_2O_5 > V_2O_4$   
~~(C)  $V_2O_5 > V_2O_4 > V_2O_3$~~       (D)  $V_2O_4 > V_2O_3 > V_2O_5$



+ive oxidation state ↑ acidic ↑

## d -BLOCK

11. Highest oxidation state of Mn is exhibited in  $Mn_2O_7$ . The correct statements

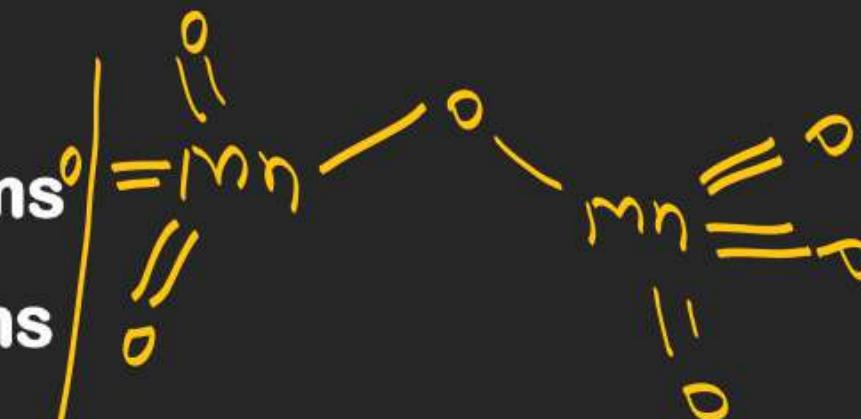
about  $Mn_2O_7$  are

- (A) Mn is tetrahedrally surrounded by oxygen atoms  
(B) Mn is octahedrally surrounded by oxygen atoms  
(C) Contains Mn – O – Mn bridge  
(D) Contains Mn – Mn bond.

Choose the correct answer from the options given below

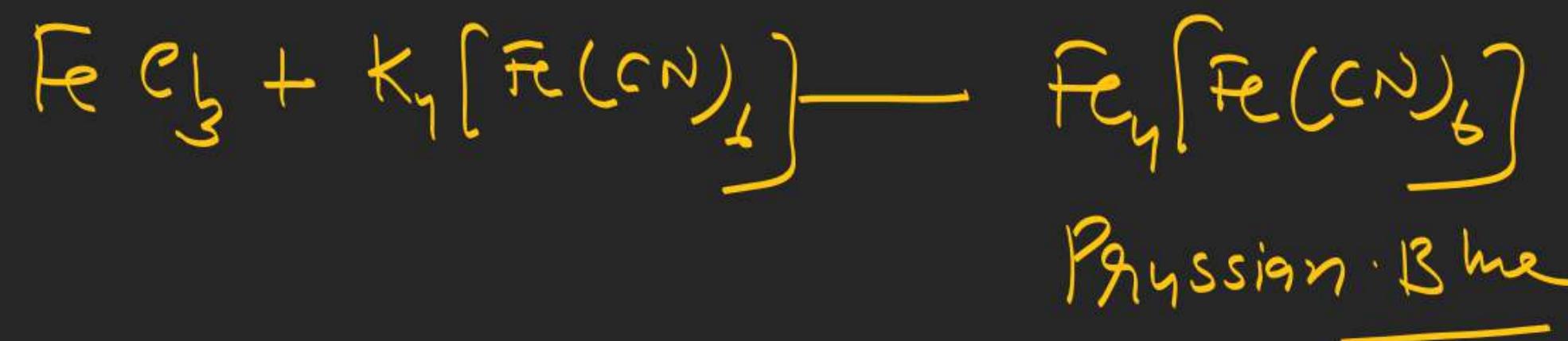
- (A) A and C only  
(C) B and D only

- (B) A and D only  
(D) B and C only



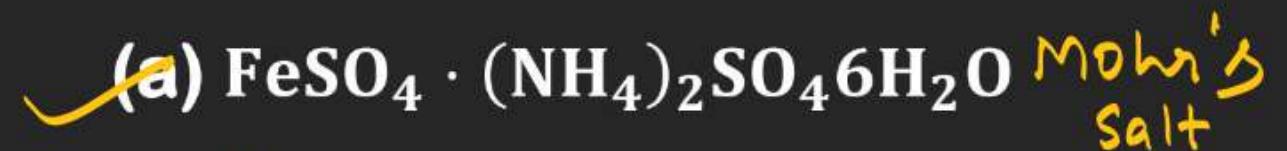
**12. A solution of  $\text{FeCl}_3$  when treated with  $\text{K}_4[\text{Fe}(\text{CN})_6]$  gives a prussian blue precipitate due to the formation of**

- (A)  $\text{K}[\text{Fe}_2(\text{CN})_6]$       (B)  $\text{Fe}[\text{Fe}(\text{CN})_6]$   
~~(C)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$~~       ~~(D)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$~~



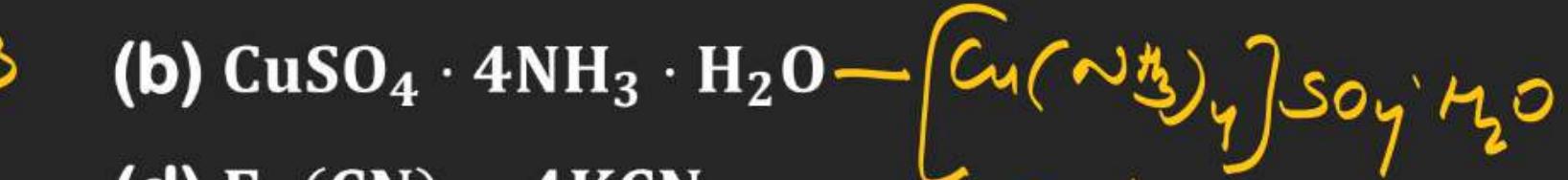
## d -BLOCK

13. Which of the following are the example of double salt?



Choose the correct answer.

- ~~(A) A and C only~~  
~~(C) A, B and D only~~



(B) Blue



14. Given below are two statements : one is labelled as Assertion (A) and the other is labelled as Reason (R).

**Assertion (A) :** Cu<sup>2+</sup> in water is more stable than Cu<sup>+</sup>.

**Reason (R) :** Enthalpy of hydration for Cu<sup>2+</sup> is much less than that of Cu<sup>+</sup>.

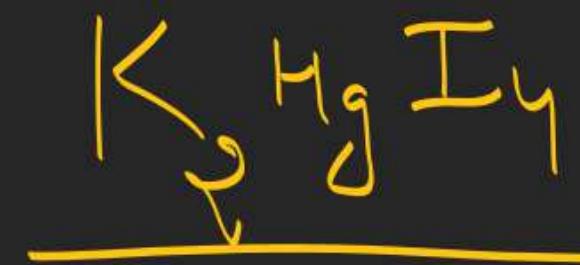
In the light of the above statements, choose the correct answer from the options given below :

- (A) Both (A) and (R) are correct and (R) is the correct explanation of (A).
- (B) (A) is correct but (R) is not correct.
- (C) (A) is not correct but ( R) is correct.
- (D) Both (A) and (R) are correct but (R) is not the correct explanation of (A).

**d -BLOCK**

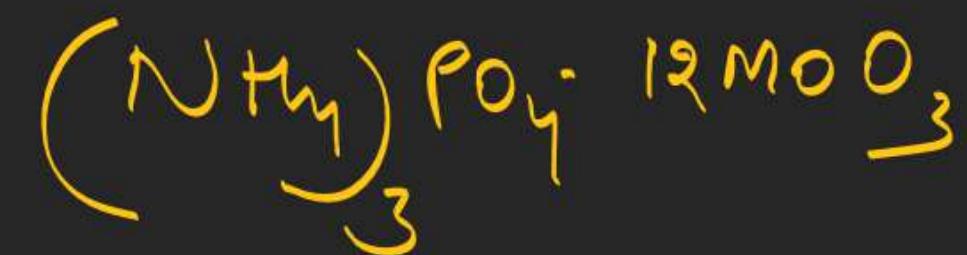
15. Which element is not present in Nessler's reagent?

- (A) Mercury
- (B) Potassium
- (C) Iodine
- (D) Oxygen

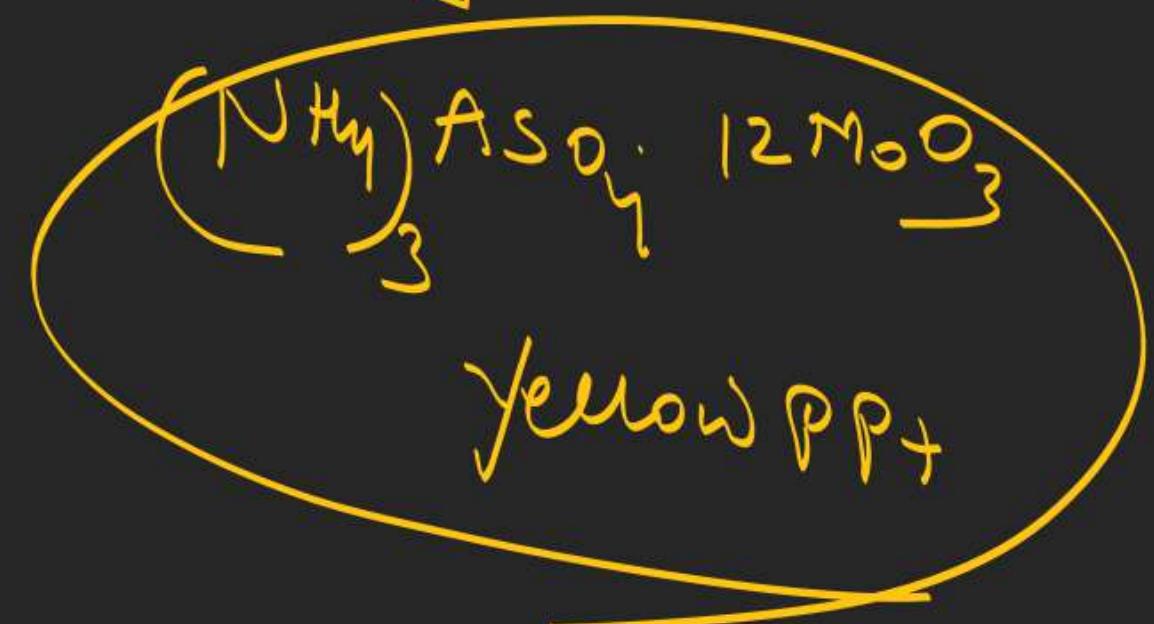


16. In ammonium - phosphomolybdate, the oxidation state of Mo is +

Salt (+6)



Canary yellow ppt



Yellow ppt

## d -BLOCK

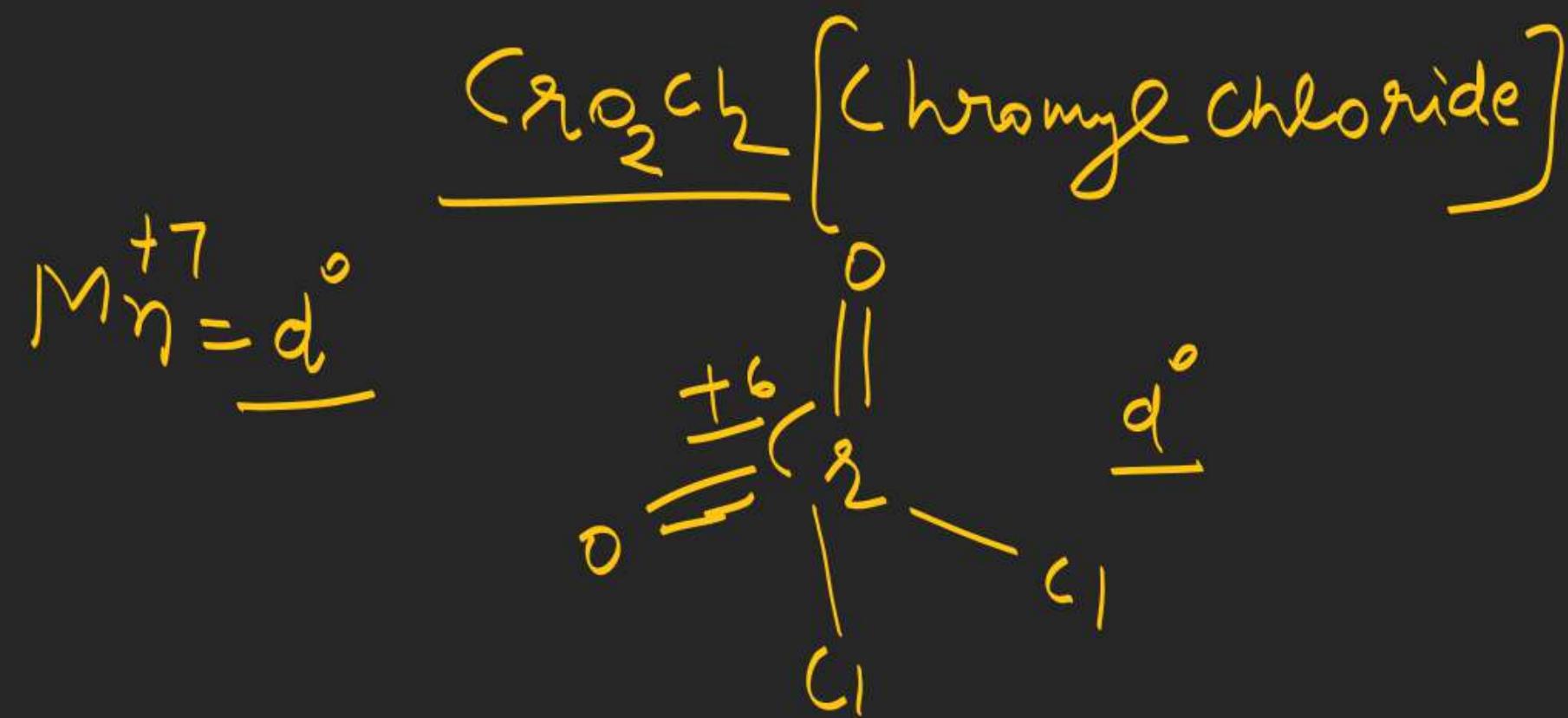
17. In chromyl chloride, the number of d-electrons present on chromium is same as in (Given at no. of Ti: 22, V: 23, Cr: 24, Mn: 25, Fe: 26 )

(A) V (IV)

(B) Mn (VII)

(C) Fe (III)

(D) Ti(III)



**18. Which halogen is known to cause the reaction given below?**






19. Given below are two statements:

**Statement I : Aqueous solution of  $K_2Cr_2O_7$  is preferred as a primary standard in volumetric analysis over  $Na_2Cr_2O_7$  aqueous solution.**

**Statement II :  $K_2Cr_2O_7$  has a higher solubility in water than  $Na_2Cr_2O_7$ . In the light of the above statements, choose the correct answer from the options given below:**

- (A) Statement I is false but Statement II is true
- (B) Both Statement I and Statement II are true
- ~~(C) Statement I is true but Statement II is false~~
- (D) Both Statement I and Statement II are false

## d -BLOCK

20. Prolonged heating is avoided during the preparation of ferrous ammonium sulphate to

- (A) Prevent hydrolysis
- (B) Prevent reduction
- (C) Prevent breaking
- (D) Prevent oxidation



d -BLOCK

**21. Which of the following statements are correct?**

~~1.51~~  
an manganese.

- (A) The  $M^{3+}/M^{2+}$  reduction potential for iron is greater than manganese.

(B) The higher oxidation states of first row d-block elements get stabilized by oxide ion

(C) Aqueous solution of  $Cr^{2+}$  can liberate hydrogen from dilute acid

(D) Magnetic moment of  $V^{2+}$  is observed between 4.4-5.2 BM

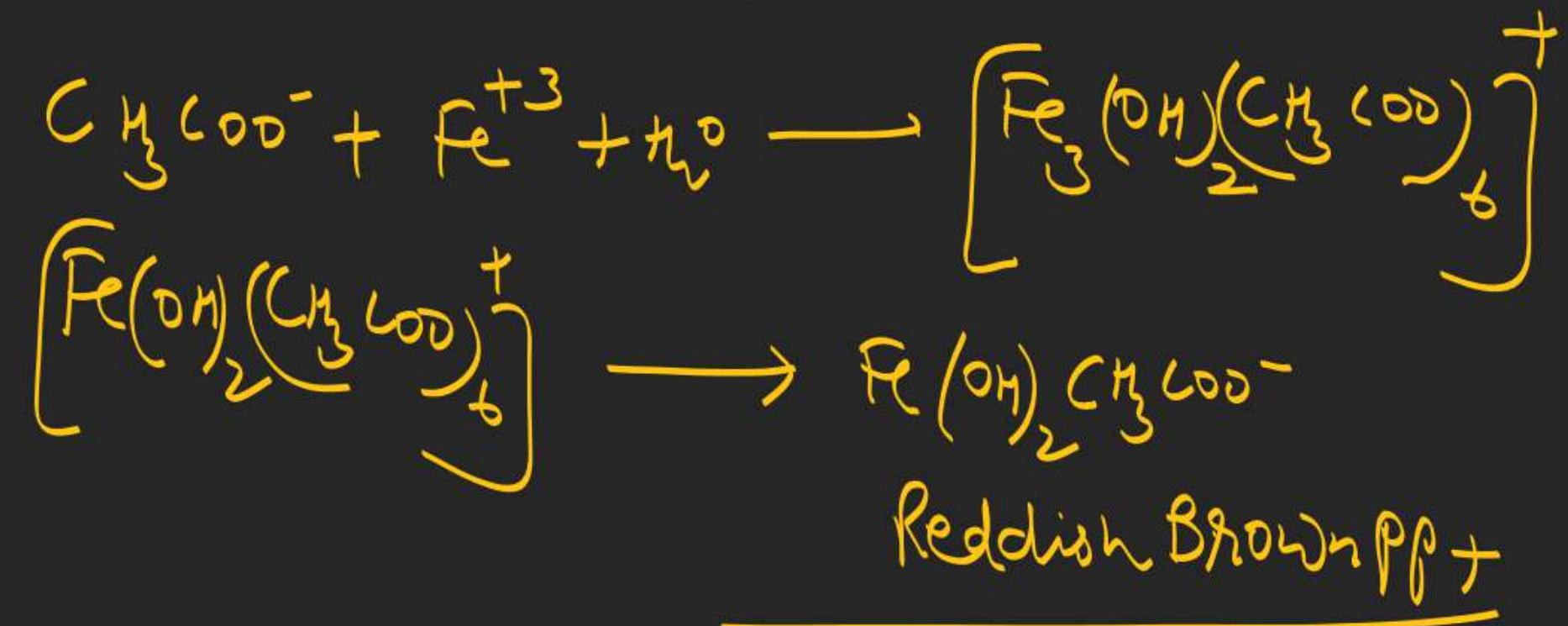
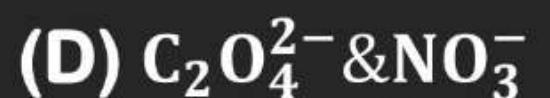
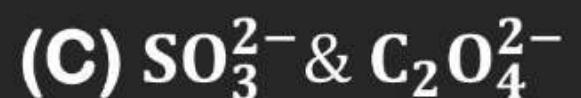
**Choose the correct answer from the options given below:**

- (A) (B), (C) only      (B) (A), (B), (D) only  
 (C) (C), (D) only      (D) (A), (B) only

$$\sqrt{+2} = 3d^3$$

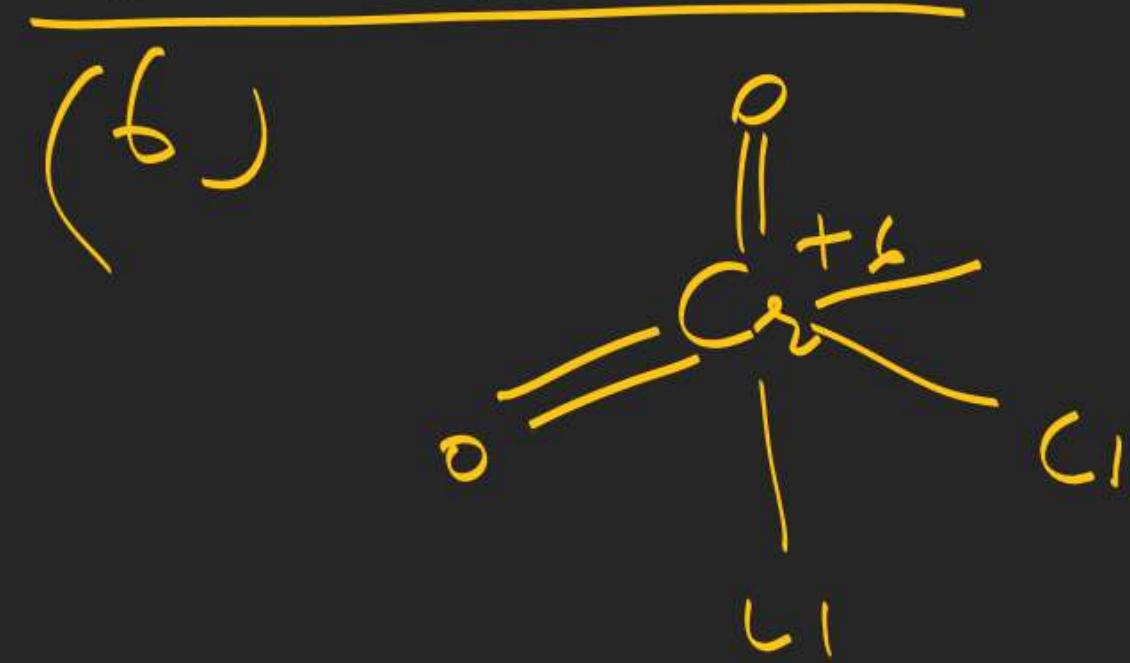
## d -BLOCK

22. When a solution of mixture having two inorganic salts was treated with freshly prepared ferrous sulphate in acidic medium, a dark brown ring was formed whereas on treatment with neutral  $\text{FeCl}_3$ , it gave deep red colour which disappeared on boiling and a brown red ppt was formed. The mixture contains



## d -BLOCK

23. In Chromyl chloride, the oxidation state of chromium is (+) \_\_\_\_\_.



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