

## d-block Element

EXERCISE-II

**Q.1 Number of electrons transferred in each case when  $\text{KMnO}_4$  acts as an oxidising agent to give  $\text{MnO}_2$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn(OH)}_3$  and  $\text{MnO}_4^{2-}$  are respectively :**

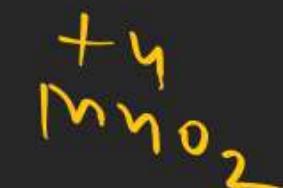
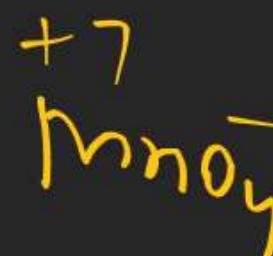
[AIEEE 2002, 3/225]

**(A) 3, 5, 4 and 1**

**(C) 1, 3, 4 and 5**

**(B) 4, 3, 1 and 5**

**(D) 5, 4, 3 and 1**



## d-block Element

2. Which of the following ions has the maximum magnetic moment?

[AIEEE 2002, 3/225]

(A) ~~Mn<sup>2+</sup>~~

(B) Fe<sup>2+</sup>

(C) Ti<sup>2+</sup>

(D) Cr<sup>2+</sup>.

$$Mn^{+2} = 3d^5$$

$$Fe^{+2} = 3d^6$$

$$Ti^{+2} = 3d^2$$

$$Cr = 3d^5 4s^1$$



$$= 3d^4$$



## d-block Element

4. What would happen when a solution of potassium chromate is treated with an excess of dilute  $\text{HNO}_3$  ?

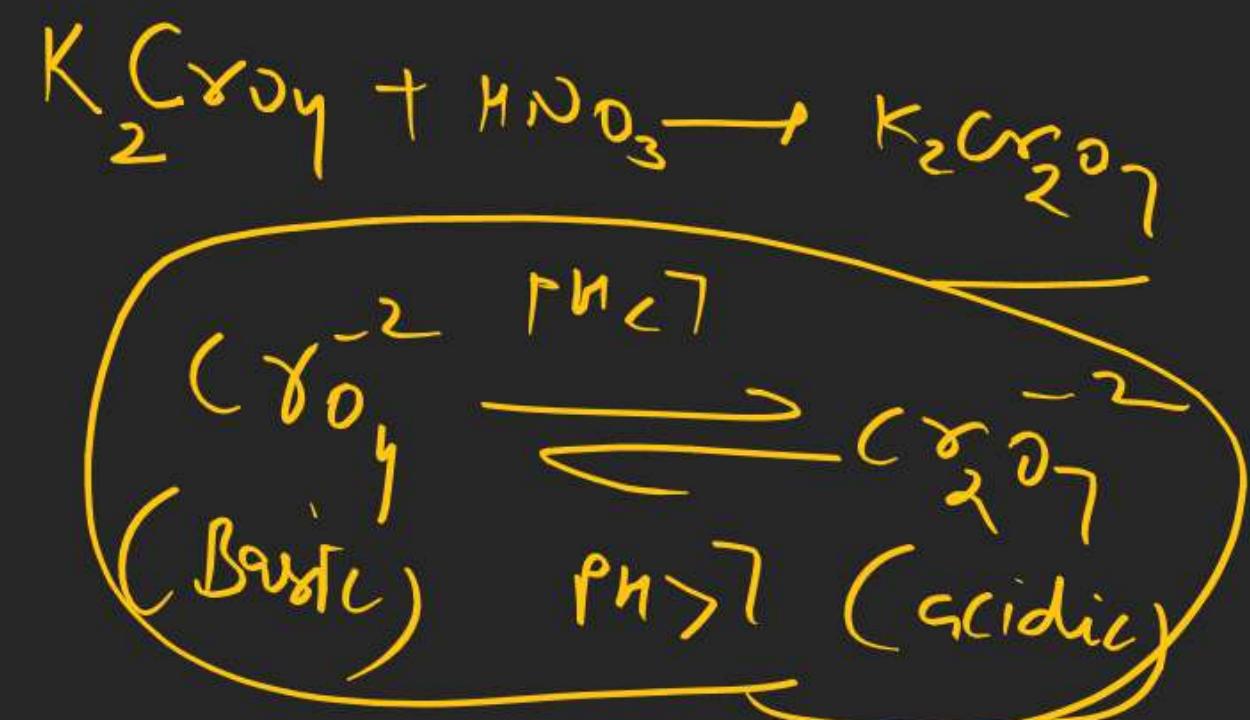
[AIEEE 2003, 3/225]

(A)  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{H}_2\text{O}$  are formed

(B)  $\text{CrO}_4^{2-}$  is reduced to +3 state of Cr

(C)  $\text{CrO}_4^{2-}$  is oxidised to +7 state of Cr

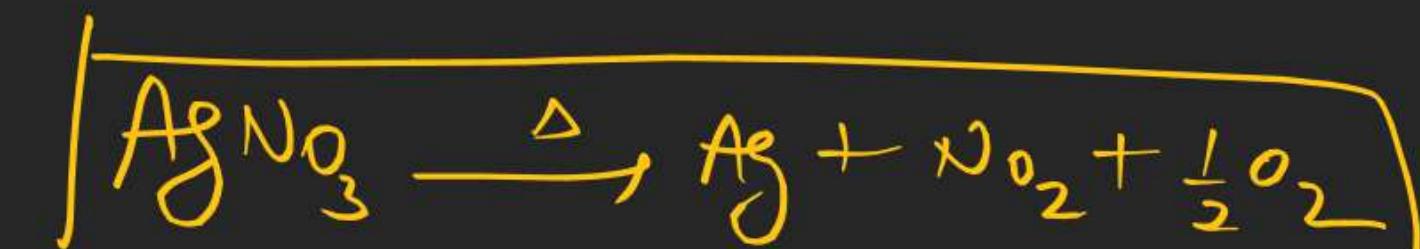
(D)  $\text{Cr}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  are formed



# d-block Element

5. Which one of the following nitrates will leave behind a metal on strong heating ?

[AIEEE 2003, 3/225]



## d-block Element

6. The atomic numbers of V, Cr, Mn and Fe are respectively 23, 24, 25 and 26 . Which one of these may be expected to have the highest second ionization enthalpy?

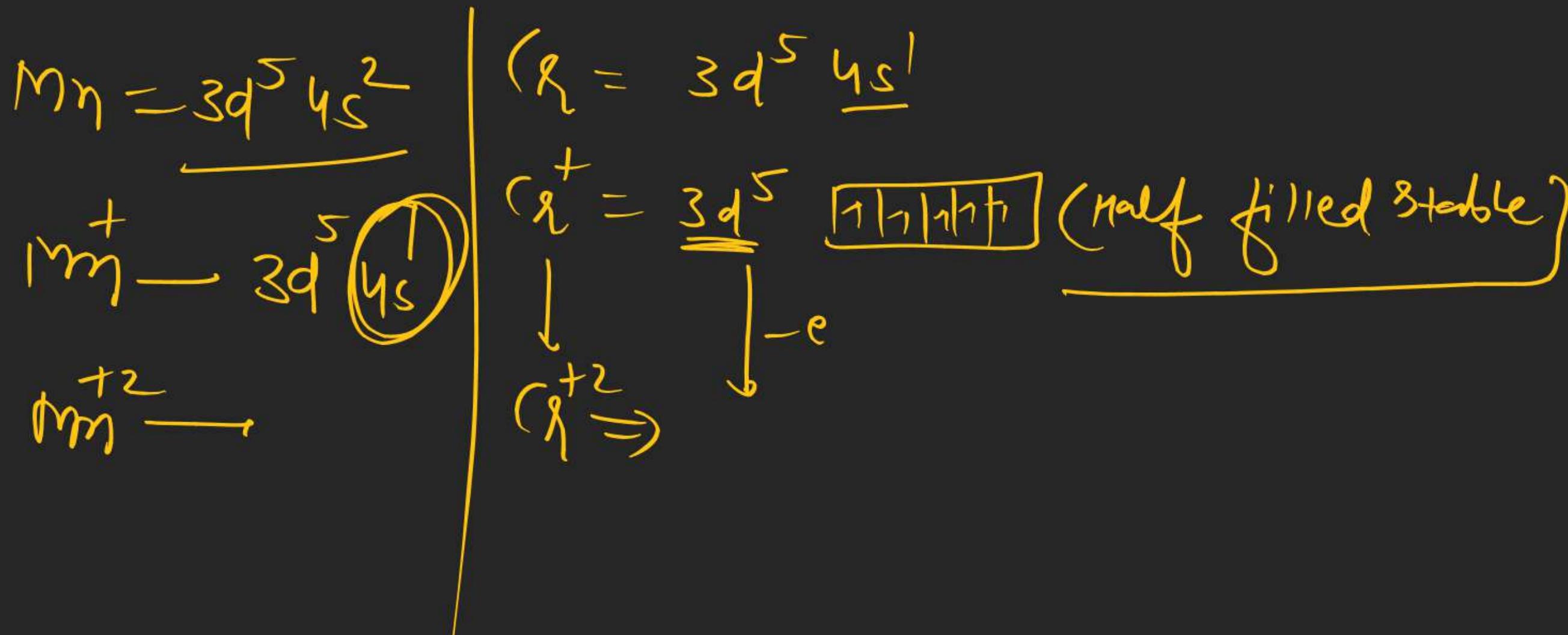
[AIEEE 2003, 3/225]

~~(A) Cr~~

(B) Mn

(C) Fe

(D) V



## d-block Element

7. Which of the following group of transition metals is called coinage metals ?

[AIEEE 2003, 3/225]

- (A) Cu, Ag, Au      (B) Ru, Rh, Pb      (C) Fe, Co, Ni      (D) Os, Ir, Pt

## d-block Element

8. The number of d-electrons retained in  $\text{Fe}^{2+}$  (At. no. Fe = 26) ions are:

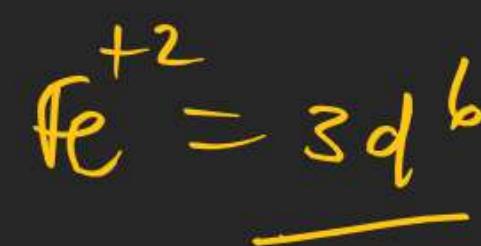
[AIEEE 2003, 3/225]

(A) 3

(B) 4

(C) 5

(D) 6



## d-block Element

9. Ammonia forms the complex ion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  with copper ions in the alkaline solutions but not in acidic solutions. What is the Statement-2 for it? [AIEEE 2003, 3/225]

- (A) In acidic solutions hydration protects copper ions
- (B) In acidic solutions protons co-ordinate with ammonia molecules forming  $\text{NH}_4^+$  ions and  $\text{NH}_3$  molecules are not available.
- (C) In alkaline solutions insoluble  $\text{Cu}(\text{OH})_2$  is precipitated which is soluble in excess of any alkali
- (D) Copper hydroxide is an amphoteric substance.



## d-block Element

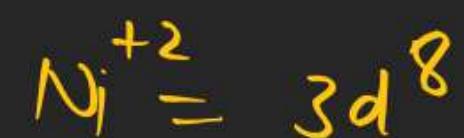
13. Which of the following factors may be regarded as the main cause of lanthanide contraction ? [AIEEE 2005, 41/2/225]

- (A) Greater shielding of 5 d electrons by 4f electrons
- (B) Poorer shielding of 5 d electron by 4f electrons
- (C) Effective shielding of one of 4f electrons by another in the sub-shell
- (D) Poor shielding of one of 4f electron by another in the sub-shell.

## d-block Element

14. The "spin-only" magnetic moment [in units of Bohr magneton, ( $\mu_B$ ) of  $\text{Ni}^{2+}$  in aqueous solution would be (atomic number of Ni = 28) [AIEEE 2006, 3/165]

- (A) 2.84      (B) 4.90      (C) 0      (D) 1.73



$$M = \sqrt{\gamma(g+2)} B \cdot M$$

$g \cdot p \cdot e$	$M$
1	1.73
2	2.80
3	3.87
4	4.90
5	5.92
6	6.92

## d-block Element

19. In context with the transition elements, which of the following statements is incorrect? *highest  $\Rightarrow$  O.S (acidic)* *lowest O.S : Basic* [AIEEE 2009, 4/144]
- (A) In the highest oxidation states, the transition metal show basic character and form cationic complexes.
- (B) In the highest oxidation states of the first five transition elements ( Sc to Mn), all the 4 s and 3 d electrons are used for bonding.
- (C) Once the  $d^5$  configuration is exceeded, the tendency to involve all the 3 d electrons in bonding decreases.
- (D) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.

## d-block Element

24. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron

**is incorrect?**



[AIEEE 2012, 4/120]

(A) Ferrous oxide is more basic in nature than the ferric oxide.

(B) Ferrous compounds are relatively more ionic than the corresponding ferric

compounds



$\text{FeCl}_3$  (Covalent More volatile)

(C) Ferrous compounds are less volatile than the corresponding ferric compounds

(D) Ferrous compounds are more easily hydrolysed than the corresponding ferric

compounds.



Charge ↑

## d-block Element

25. Which of the following arrangements **does not represent the correct order of the property stated against it?**

[JEE(Main) 2013, 4/120]

- (A)  ~~$V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$~~  : paramagnetic behaviour
- (B)  $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$  : ionic size
- (C)  $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$  : stability in aqueous solution
- (D)  $Sc < Ti < Cr < Mn$  : number of oxidation states



U.P.-e

1	1	1	1	1
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s



g

5	1	1	1	1
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## d-block Element

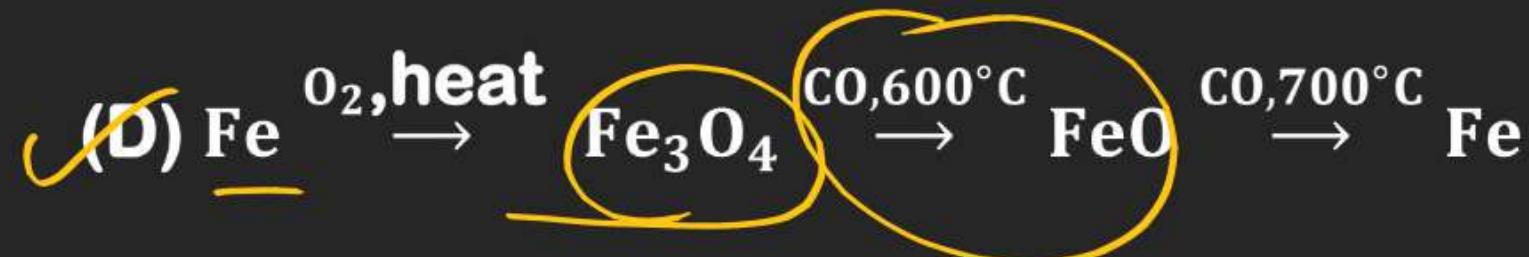
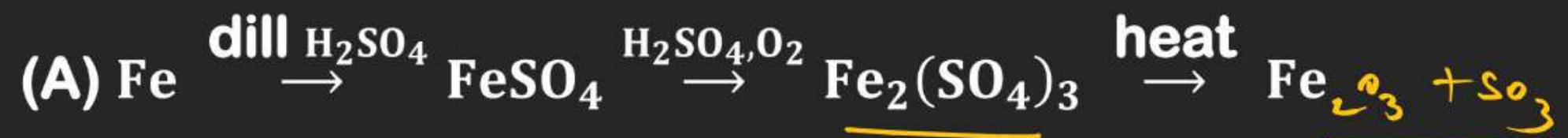
26. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest  $E_{M^{3+}/M^{2+}}^0$  value ?

[JEE(Main) 2013, 4/120]

- (A) Cr(Z = 24)      (B) Mn(Z = 25)      (C) Fe(Z = 26)      (D) ~~Co(Z = 27)~~

## d-block Element

27. Which series of reactions correctly represents chemical relations related to iron and its compound? [JEE(Main) 2014, 4/120]

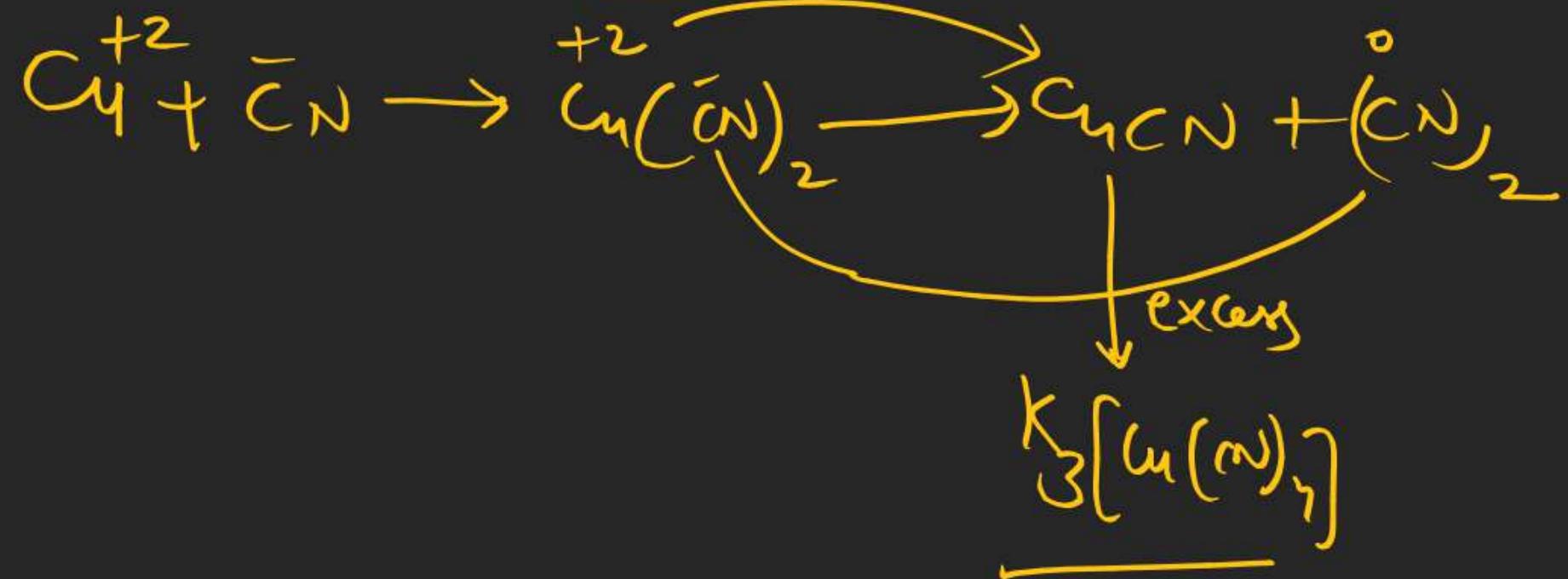


below  
710°C

## d-block Element

28. The equation which is balanced and represents the correct product(s) is :

[JEE(Main) 2014, 4/120]

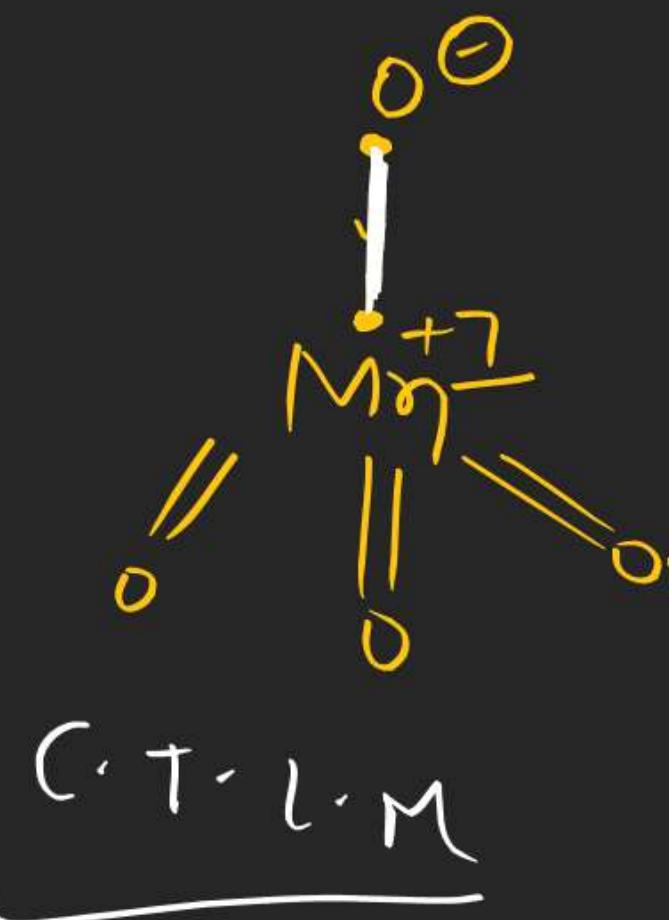


## d-block Element

29. The colour of  $\text{KMnO}_4$  is due to :

[JEE(Main) 2015, 4/120]

- (A)  $M \rightarrow L$  charge transfer transition      (B) d – d transition  
~~(C)  $L \rightarrow M$  charge transfer transition      (D)  $\sigma - \sigma^*$  transition~~



## d-block Element

30. When  $XO_2$  is fused with an alkali metal hydroxide in presence of an oxidizing agent such as  $KNO_3$ ; a dark green product is formed which disproportionates in acidic solution to afford a dark purple solution. X is :

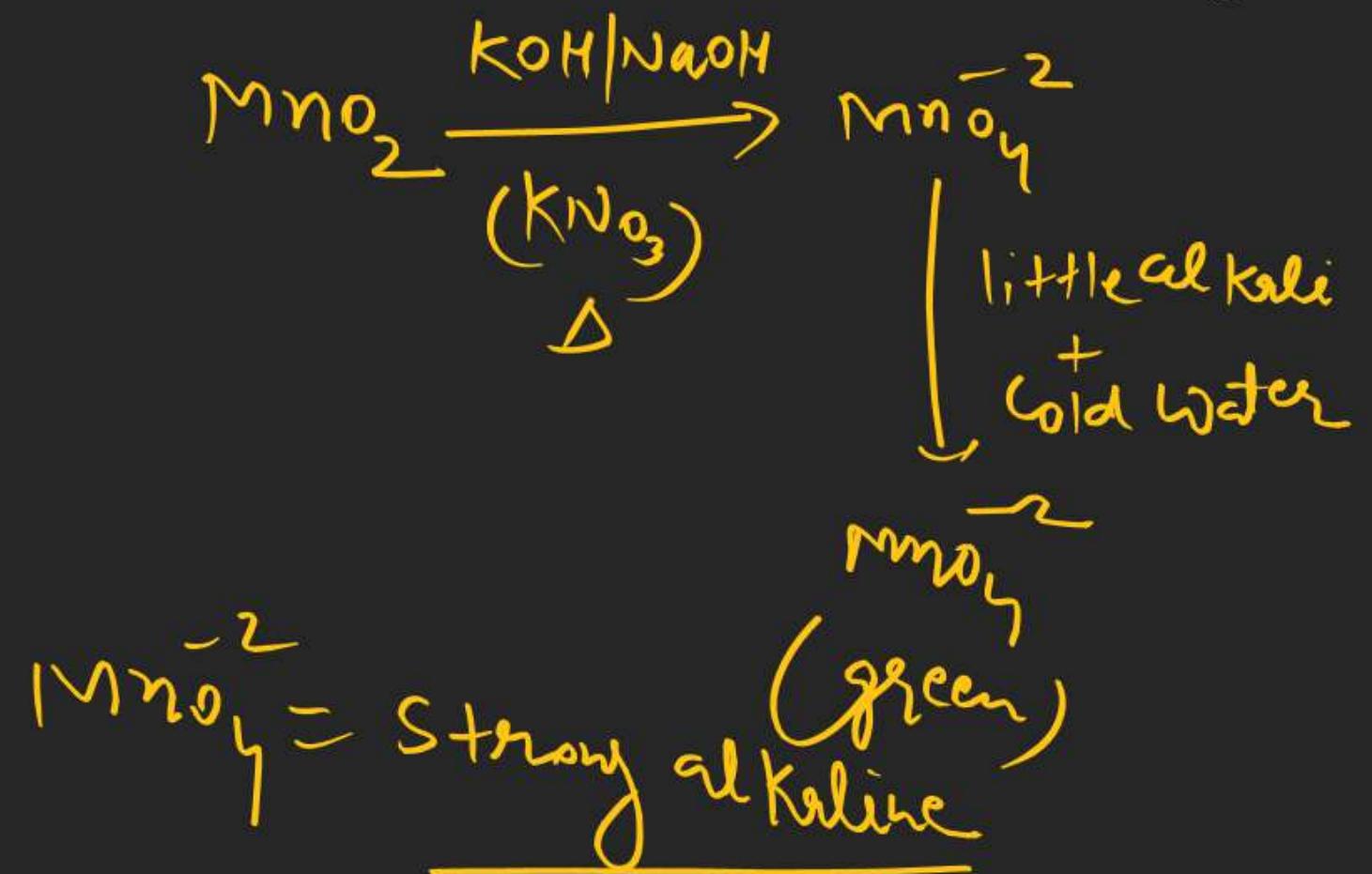
[JEE(Main) 2018(online)]

(A) Ti

(B) V

(C) Cr

(D) Mn



## d-block Element

31. The transition element that has lowest enthalpy of atomisation is : [JEE-Main 2019]

(A) Zn

(B) Cu

(C) Fe

(D) V

## d-block Element

33. The electrolytes usually used in the electroplating of gold and silver, respectively, are : [JEE-Main 2019]

- (A)  $[\text{Au}(\text{CN}_2)]^-$  and  $[\text{Ag}(\text{CN})_2]^-$
- (B)  $[\text{Au}(\text{NH}_3)_2]^+$  and  $[\text{Ag}(\text{CN})_2]^-$
- (C)  $[\text{Au}(\text{CN}_2)]^-$  and  $[\text{Ag}(\text{Cl})_2]^-$
- (D)  $[\text{Au}(\text{OH})_4]^-$  and  $[\text{Ag}(\text{OH})_2]^-$

## d-block Element

34. The element that usually does NOT show variable oxidation states is :

[JEE-Main 2019]

- (A) Cu  
 $\downarrow$   
 $Cu^+$   
 $Cu^{+2}$
- (B) Sc
- (C) V  
 $\nearrow^{+3}$   
 $\nearrow^{+5}$   
 $Sc^{+3}$
- (D) Ti  
 $\nearrow^{+2}$   
 $\nearrow^{+4}$

## d-block Element

35. The correct order of the first ionization enthalpies is:

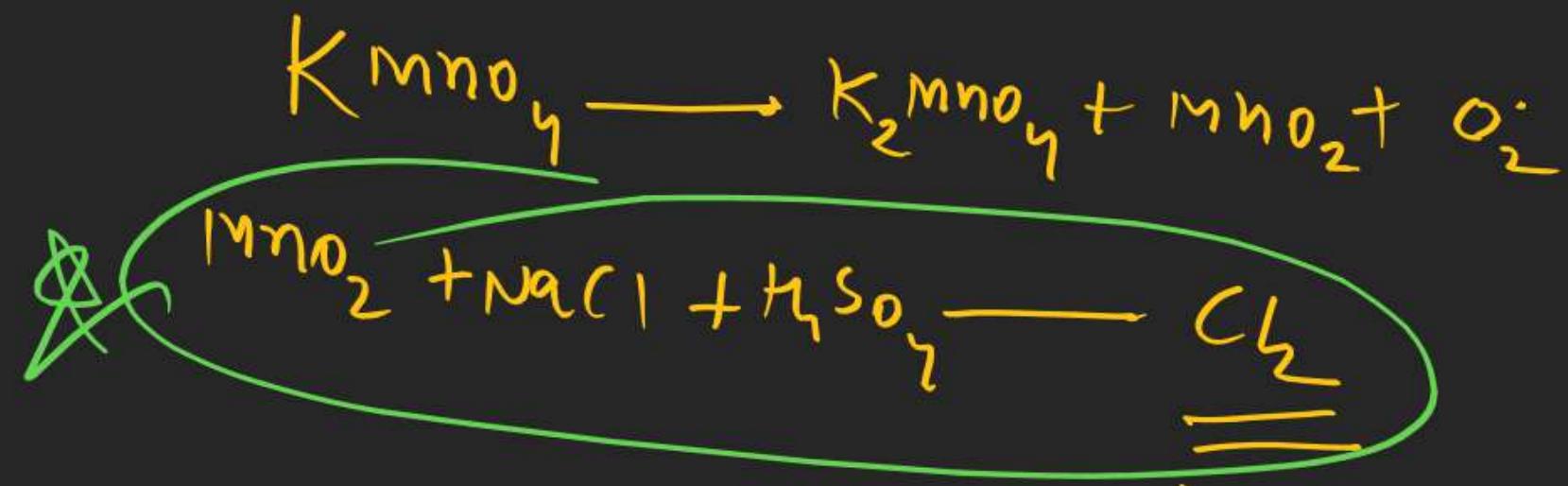
[JEE-Main 2019]

- (A) Ti < Mn < Zn < Ni
- ~~(B) Ti < Mn < Ni < Zn~~
- (C) Mn < Ti < Zn < Ni
- (D) Zn < Ni < Mn < Ti

## d-block Element

36. Thermal decomposition of a Mn compound (X) at 513K results in compound Y,  $\text{MnO}_2$  and a gaseous product MnO<sub>2</sub> reacts with NaCl and concentrated  $\text{H}_2\text{SO}_4$  to give pungent gas Z. X, Y, and Z, respectively, are: [Main April 12, 2019]

- (A)  $\text{KMnO}_4$ ,  $\text{K}_2\text{MnO}_4$  and  $\text{Cl}_2$       (B)  $\text{K}_2\text{MnO}_4$ ,  $\text{KMnO}_4$  and  $\text{SO}_2$   
(C)  $\text{K}_3\text{MnO}_4$ ,  $\text{K}_2\text{MnO}_4$  and  $\text{Cl}_2$       (D)  $\text{K}_2\text{MnO}_4$ ,  $\text{KMnO}_4$  and  $\text{Cl}_2$



## d-block Element

37. Match the catalysts (Column-I) with products (Column-II)

[Main April 9, 2019]

**Column-1****(Catalyst)**(A)  $V_2O_5$ (B)  $TiCl_4/Al(Me)_3$ (C)  $PdCl_2$ 

(D) Iron Oxide

**Column-2****(Product)**

(i) Polyethylene

(ii) ethanol

(iii)  $H_2SO_4$ (iv)  $NH_3$ 

(A) (A)-(iii); (B)-(iv); (C)-(i); (D)-(ii)

(C) (A)-(iii); (B)-(i); (C)-(ii); (D)-(iv)

(B) (A)-(ii); (B)-(iii); (C)-(i); (D)-(iv)

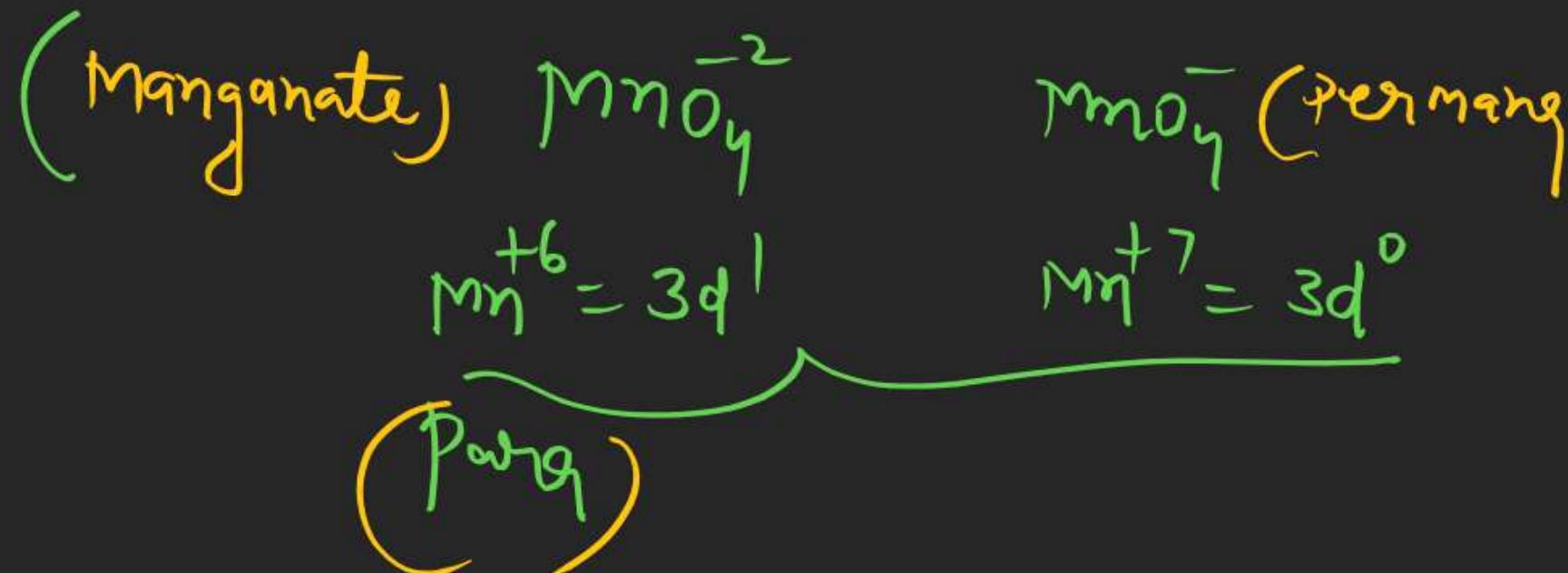
(D) (A)-(iv); (B)-(iii); (C)-(ii); (D)-(i)

## d-block Element

38. The incorrect statement is:

[Main Sep. 03, 2020]

- (A) Manganate and permanganate ions are tetrahedral
- (B) In manganate and permanganate ions, the  $\pi$ -bonding takes place by overlap of p-orbitals of oxygen and d orbitals of manganese
- ~~(C) Manganate and permanganate ions are paramagnetic~~
- (D) Manganate ion is green in colour and permanganate ion is purple in colour



## d-block Element

39. The third ionization enthalpy is minimum for:

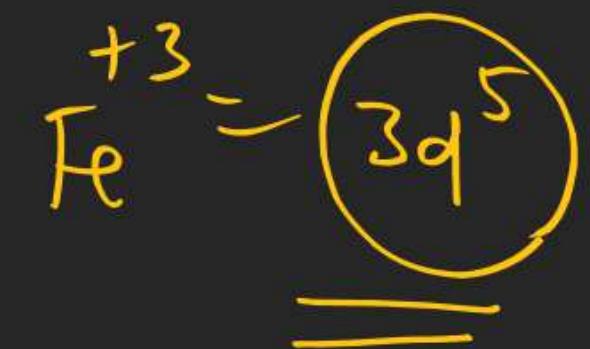
[Main Jan. 08, 2020]

(A) Co

~~(B) Fe~~

(C) Ni

(D) Mn



7 s	2	2	2	2	2	2	2	2	1
5 d	1	2	3	4	5	6	7	8	10

**General Characteristics:**

- (i) **Metallic character:** They are all metal and good conductor of heat & electricity
- (ii) **Electronic configuration:**  $(n - 1)d^{1-10} ns^{1-2}$

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Others are as usual			$4s^1$				$4s^1$		$3d^{10}$

**(iii) M.P.**

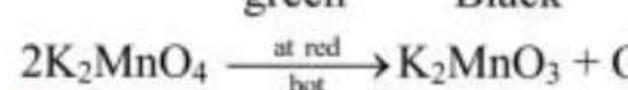
Cr }  $\rightarrow$  Maximum  
 Mo } 6 no. of unpaired e<sup>-</sup>s  
 W } Are involved in metallic bonding

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

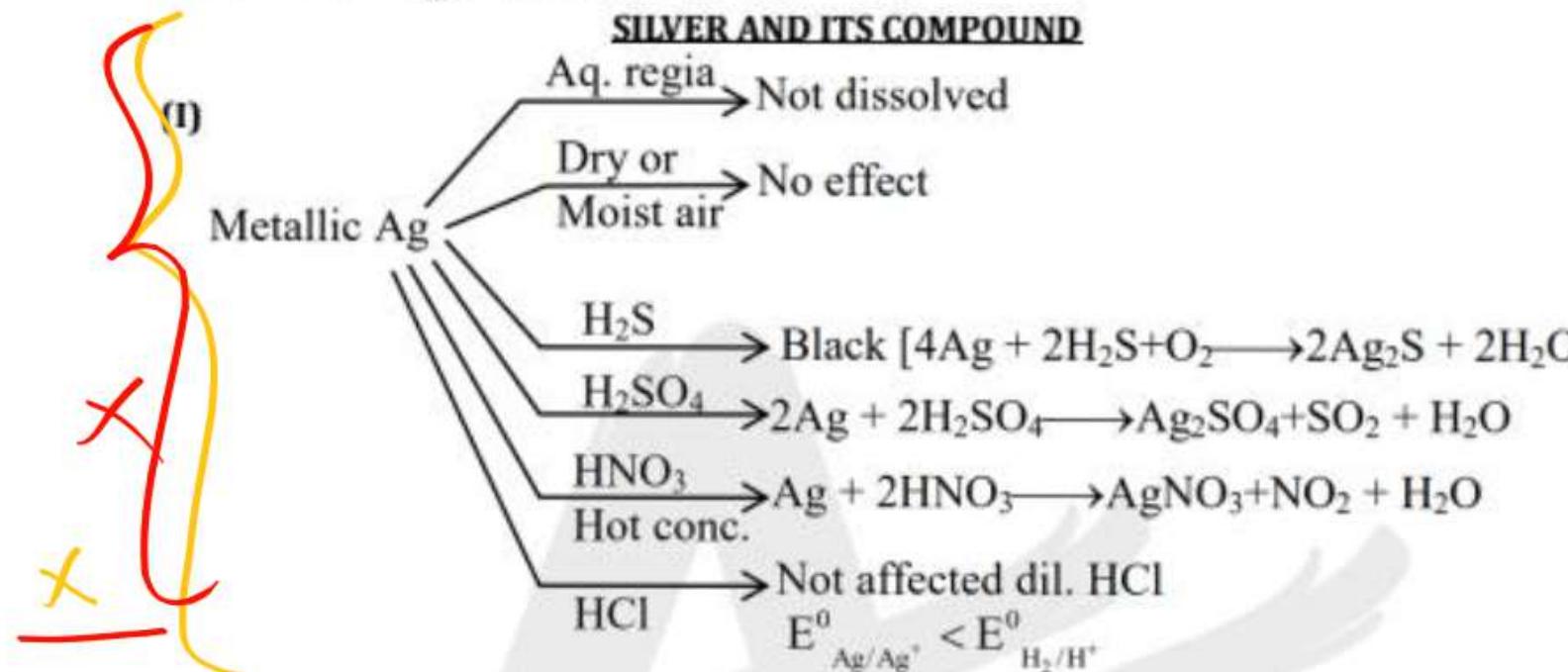
$\Delta_1 H^\ominus / \text{kJ mol}^{-1}$								
$\Delta_1 H^\Theta$	II	1235	1309	1414	1592	1509	1561	1644
	III	2393	2657	2833	2990	3260	2962	3243

### 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).
- (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.,  $\text{V}^{\text{II}}$ ,  $\text{V}^{\text{III}}$ ,  $\text{V}^{\text{IV}}$ ,  $\text{V}^{\text{V}}$ .

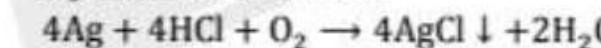


### SILVER AND ITS COMPOUND

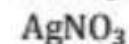
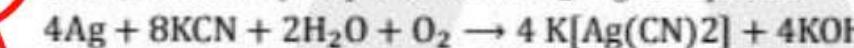


Hence in presence of  $\text{O}_2$ ,

Ag reacts with dil. HCl



In the same way in presence of  $\text{O}_2$ , Ag complexes with NaCN/KCN.



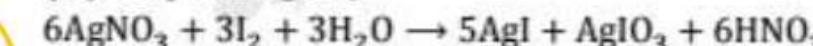
**Preparation:** Reaction of Ag with dilute  $\text{HNO}_3$  or conc.  $\text{HNO}_3$ .

**Properties:**

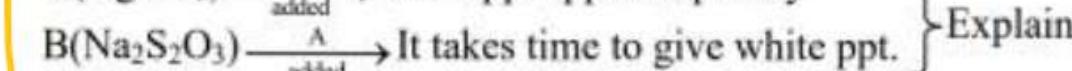
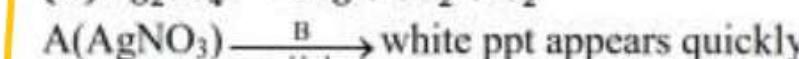
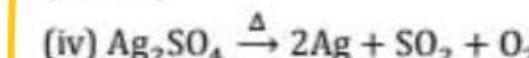
(i) It is called as lunar caustic because in contact with skin it produces burning sensation like that of caustic soda with the formation of finely divided silver (black colour)

(ii) Thermal decomposition :

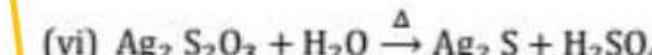
(iii) Props. of  $\text{AgNO}_3$



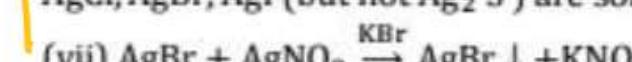
(excess)



} Explain



$\text{AgCl}, \text{AgBr}, \text{AgI}$  (but not  $\text{Ag}_2\text{S}$ ) are soluble in  $\text{Na}_2\text{S}_2\text{O}_3$  forming  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$  complexes

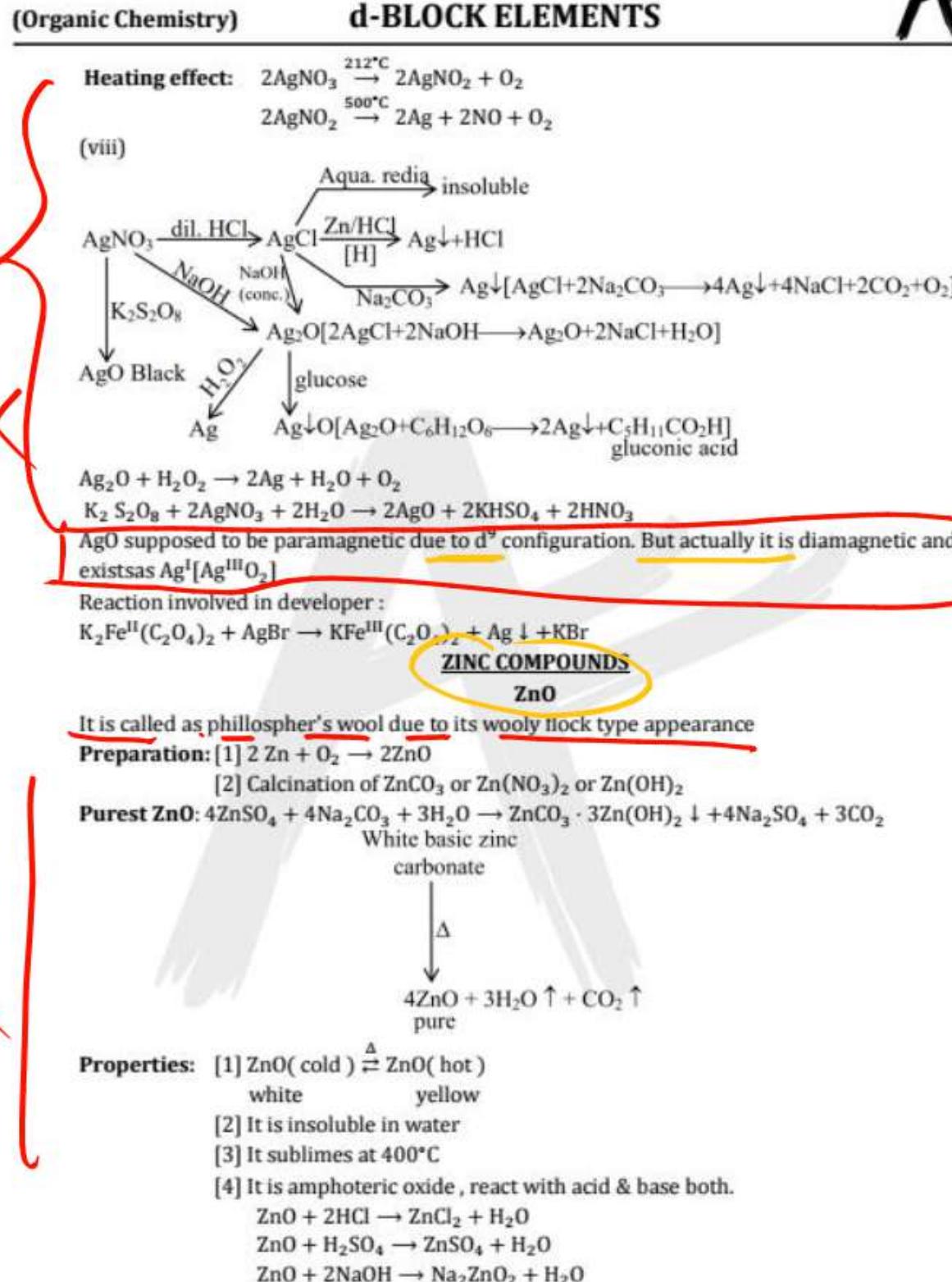


Pale yellow

$\text{Ag} = 3d^0 4s^1$

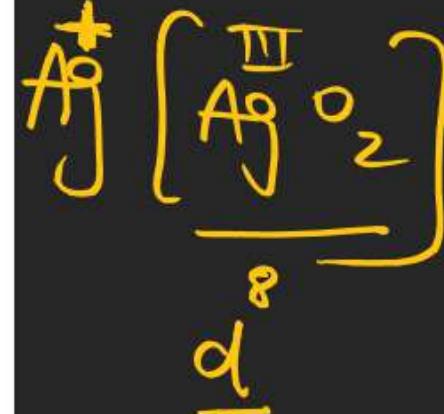
$\text{Ag}^+ = 4d^1 5s^1$

$\text{Ag}^+ = 4d^1$



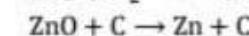
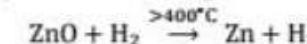
it is supp.

$\text{Ag}^{\text{O}}$  = Paramag  
but it is  
 $d^{10}$  diamag.

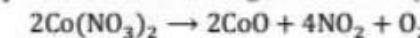




[5]  $\text{ZnO} \rightarrow \text{Zn}$  by  $\text{H}_2\&\text{C}$



[6] It forms Rinmann's green with  $\text{Co}(\text{NO}_3)_2$

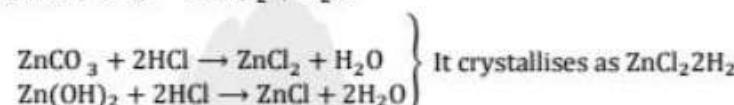


Rinmann's green

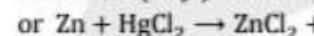
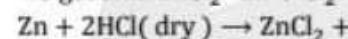
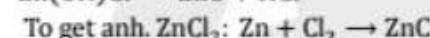
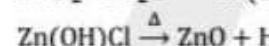
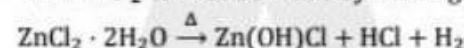
- Uses:** (1) As white pigment, it is superior than white lead because it does not turn into black  
 (2) Rinmann's green is used as green pigment  
 (3) It is used as zinc ointment in medicine



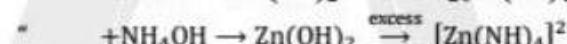
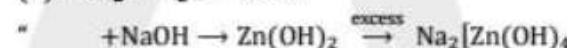
**Preparation:**  $\text{ZnO} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2\text{O}$



Anh.  $\text{ZnCl}_2$  cannot be made by heating  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$  because



**Properties:** (i) It is deliquescent white solid (when anhydrous)



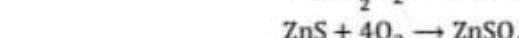
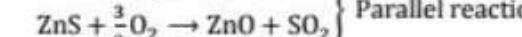
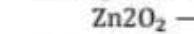
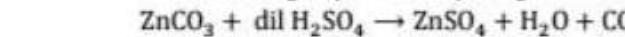
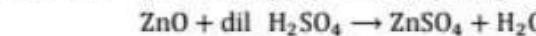
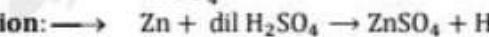
**Uses:** [1] Used for impregnating timber to prevent destruction by insects

[2] As dehydrating agent when anhydrous

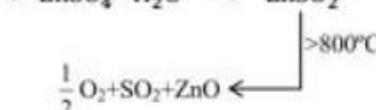
[3]  $\text{ZnO} \cdot \text{ZnCl}_2$  used in dental filling



**Preparation:**  $\rightarrow$



**Properties:**  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{39-70^\circ\text{C}} \text{ZnSO}_4 \cdot 6\text{H}_2\text{O} \xrightarrow{>70^\circ\text{C}} \text{ZnSO}_4 \cdot \text{H}_2\text{O} \xrightarrow{>280^\circ\text{C}} \text{ZnSO}_2$





- Uses:**
- [1] in eye lotion
  - [2] Lithophane making ( $\text{ZnS} + \text{BaSO}_4$ ) as white pigment

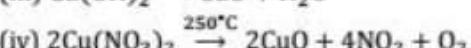
#### COPPER COMPOUNDS

##### $\text{CuO}$

**Preparation:** (i)  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \xrightarrow{\Delta} 2\text{CuO} + \text{H}_2\text{O} + \text{CO}_2$  (Commercial process)

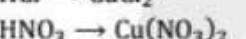
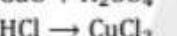
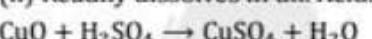
Malachite Green

(native Cu-carbonate)

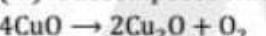


**Properties:** (i)  $\text{CuO}$  is insoluble in water

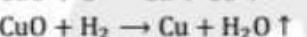
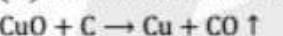
(ii) Readily dissolves in dil. Acids



(iii) It decomposes when heated above  $1100^\circ\text{C}$



(iv)  $\text{CuO}$  is reduced to Cu by  $\text{H}_2$  or C under hot condition



##### $\text{CuCl}_2$

**Preparation:**  $\rightarrow \text{CuO} + 2\text{HCl}$  (conc.)  $\rightarrow \text{CuCl}_2 + \text{H}_2\text{O}$



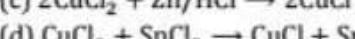
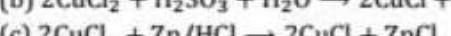
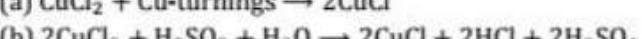
**Properties:**  $\rightarrow$  (i) It is crystallised as  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  of Emerald green colour

(ii) dil. solution in water is blue in colour due to formation of  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  complex.

(iii) conc. HCl or KCl added to dil. solution of  $\text{CuCl}_2$  the colour changes into yellow, owing to the formation of  $[\text{CuCl}_4]^{2-}$

(iv) The conc. aq. solution is green in colour having the two complex ions in equilibrium  $2[\text{Cu}(\text{H}_2\text{O})_4]\text{Cl}_2 \rightleftharpoons [\text{Cu}(\text{H}_2\text{O})_4]^{2+} + [\text{CuCl}_4]^{2-} + 4\text{H}_2\text{O}$

(v)  $\text{CuCl}_2 \rightarrow \text{CuCl}$  by no. of reagents



$\text{CuF}_3 \cdot 2\text{H}_2\text{O} \rightarrow$  light blue      Anh.  $\text{CuCl}_2$  is dark brown mass obtained

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow$  green      By heating  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  at  $150^\circ\text{C}$  in presence  
of HCl vap.

$\text{CuBr}_2 \rightarrow$  almost black



**Preparation:** → CuSO<sub>4</sub>

$$\text{CuO} + \text{H}_2\text{SO}_4(\text{dil}) \rightarrow \text{CuSO}_4 + \text{H}_2\text{O}$$

$$\text{Cu(OH)}_2 + \text{H}_2\text{SO}_4(\text{dil}) \rightarrow \text{CuSO}_4 + 2\text{H}_2\text{O}$$

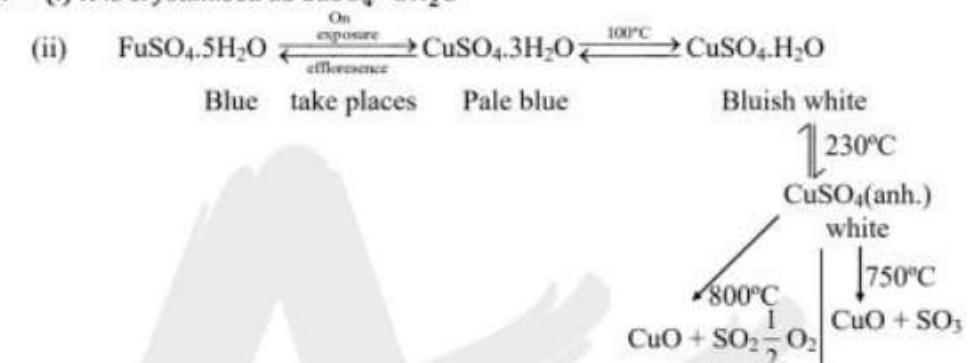
$$\text{Cu(OH)}_2 \cdot \text{CuCO}_3 + \text{H}_2\text{SO}_4(\text{dil}) \rightarrow \text{CuSO}_4 + 3\text{H}_2\text{O} + \text{CO}_2$$

$$\text{Cu} + \text{H}_2\text{SO}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CuSO}_4 + \text{H}_2\text{O} [\text{Commercial scale}]$$

(Scrap)

Cu + dil. H<sub>2</sub>SO<sub>4</sub> → no reaction (Cu is below H in electrochemical series)

**Properties:** → (i) It is crystallised as CuSO<sub>4</sub> · 5H<sub>2</sub>O



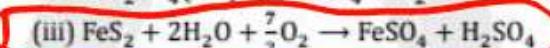
(iii) Revision with all others reagent

#### IRON COMPOUNDS

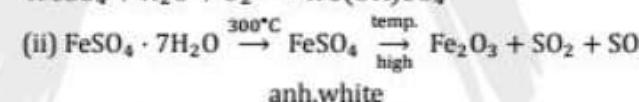
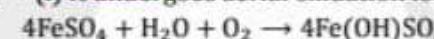
##### FeSO<sub>4</sub> · 7H<sub>2</sub>O

**Preparation:** → (i) Scrap Fe + H<sub>2</sub>SO<sub>4</sub> → FeSO<sub>4</sub> + H<sub>2</sub>↑ (dil.)

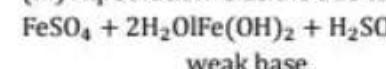
(ii) From Kipp's waste



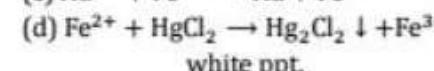
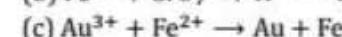
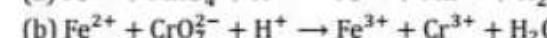
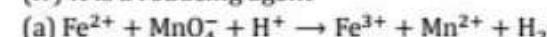
**Properties:** → (i) It undergoes aerial oxidation forming basic ferric sulphate



(iii) Aq. solution is acidic due to hydrolysis



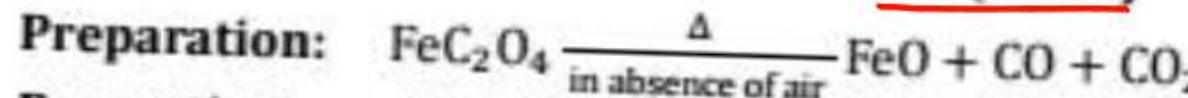
(iv) It is a reducing agent



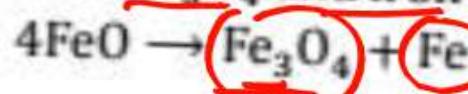
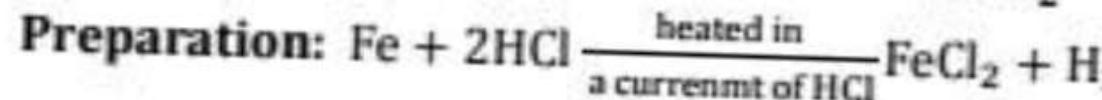
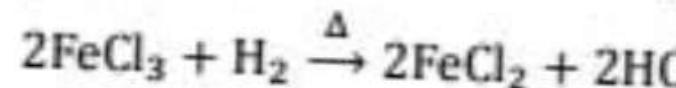
(v) It forms double salt. Example (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> · FeSO<sub>4</sub> · 6H<sub>2</sub>O



AK

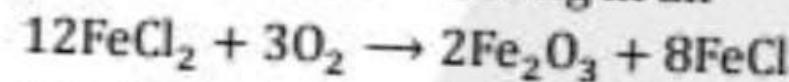
**FeO(Black)**

**Properties:** It is stable at high temperature and on cooling slowly disproportionates into  $\text{Fe}_3\text{O}_4$  and iron

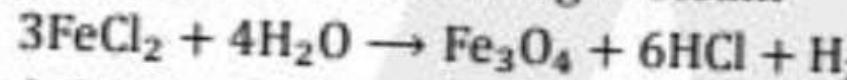
**FeCl<sub>2</sub>****OR**

**Properties:** → (i) It is deliquescent in air like  $\text{FeCl}_3$   
(ii) It is soluble in water, alcohol and ether also because it is suffici Covalent in nature  
(iii) It volatilises at about  $1000^\circ\text{C}$  and vapour density indicates the presen of  $\text{Fe}_2\text{Cl}_4$ .  
Above  $1300^\circ\text{C}$  density becomes normal

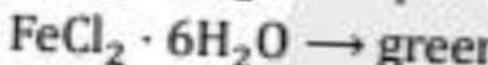
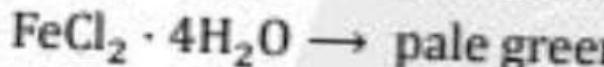
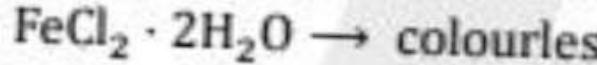
(iv) It oxidises on heating in air



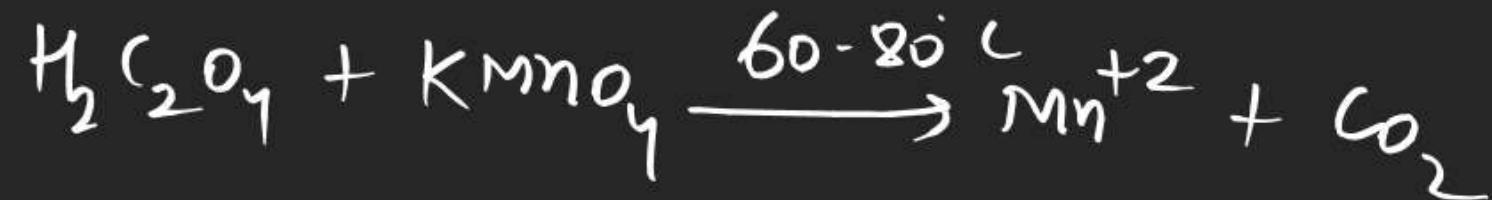
(v)  $\text{H}_2$  evolves on heating in steam



(vi) It can exist as different hydrated form



feCl<sub>2</sub>

sol

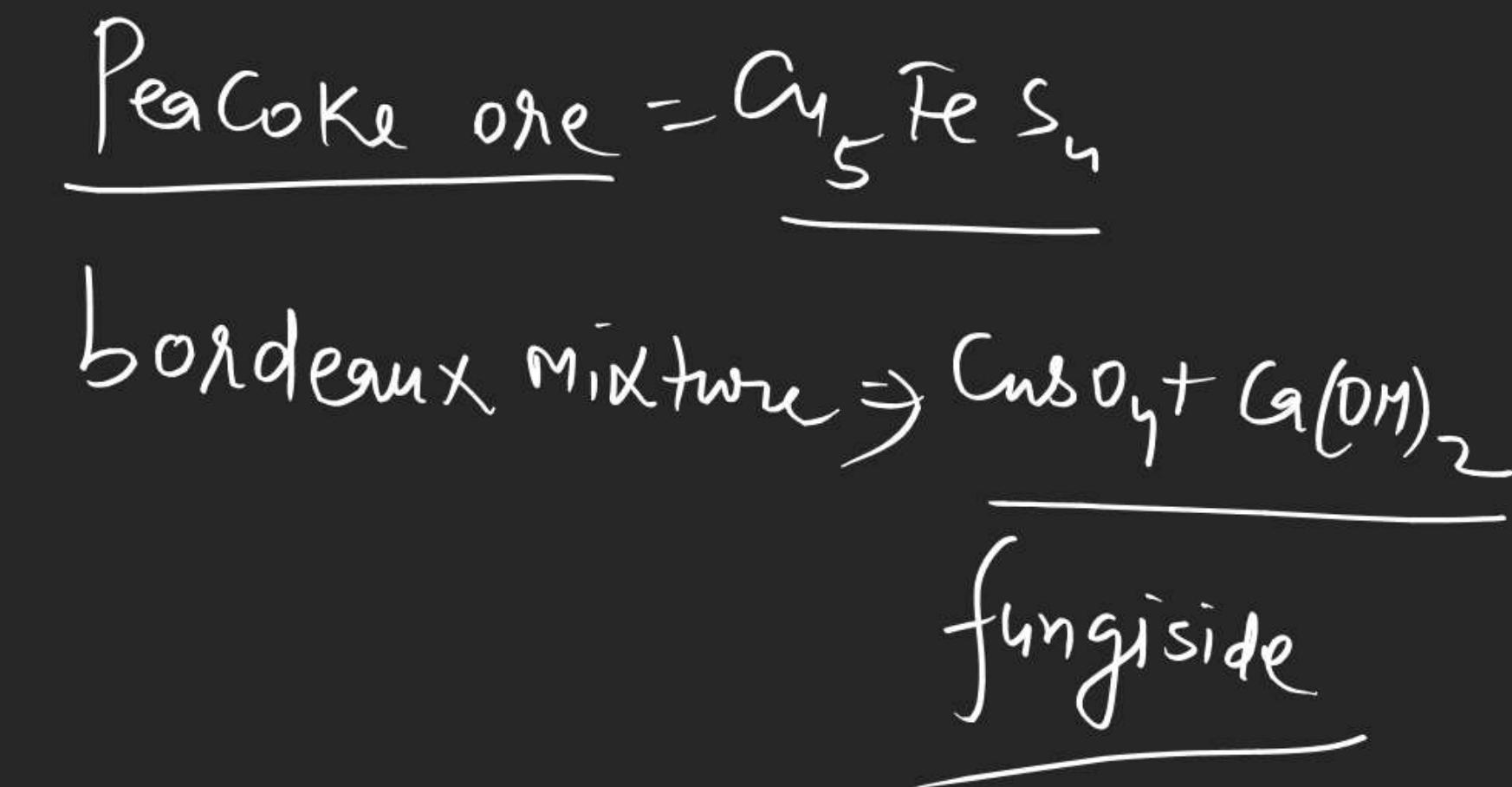
Initially this reaction needs temp.  
to start, once reaction start  
then there is no req. of heating  
because  $\text{Mn}^{+2}$  acts as Auto catalyst.  
and  $\text{KMnO}_4$  act as self indicator.

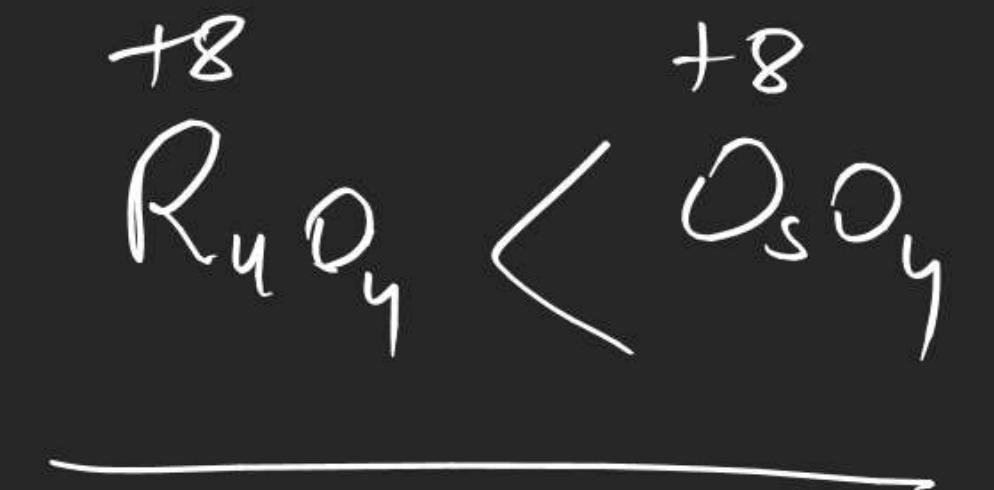
Coinage metal

Cu  
Ag  
Au

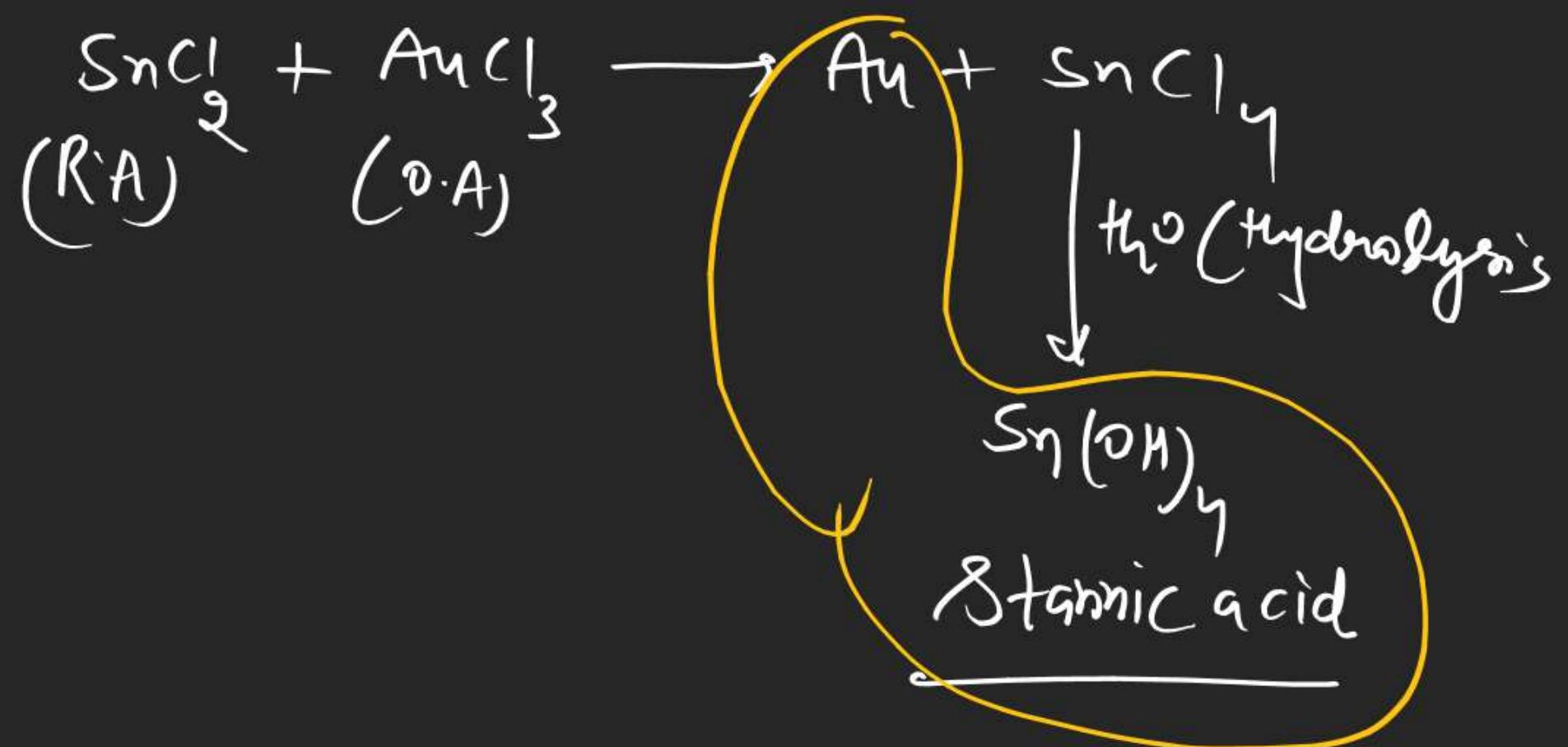
HgS = Vermilion

Ayurvedic, Yunanai medicines





Purple of Cassius



100% Au = 24 Carat

100% Ag = 1000 fine silver