

## TRANSITION ELEMENTS

Definition: They are 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.

## 1st SERIES

	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

## 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

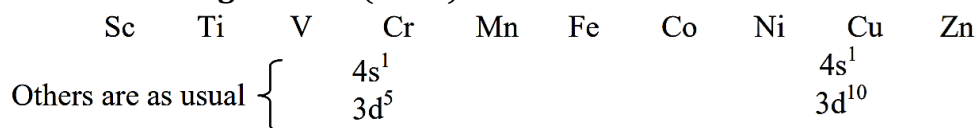
## 4th SERIES

	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

## 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.**

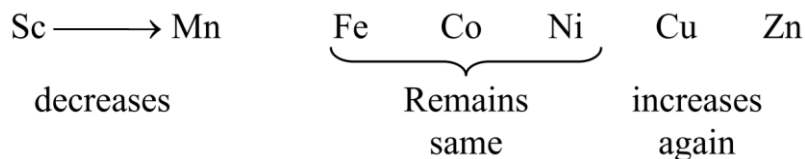
Cr }  $\longrightarrow$  Maximum  
 Mo } 6 no. of unpaired  $e^-$ s  
 W } Are involved in metallic bonding

Zn } Lowest m.p.  
 Cd } Due to no unpaired  $e^-$   
 Hg } For metallic bonding

## (Organic Chemistry)

## d-BLOCK ELEMENTS

## (iv) Variation in atomic radius:



## (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 Zn has highest.

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>	3d <sup>2</sup> 4s <sup>2</sup>	3d <sup>3</sup> 4s <sup>2</sup>	3d <sup>5</sup> 4s <sup>2</sup>	3d <sup>5</sup> 4s <sup>2</sup>	3d <sup>6</sup> 4s <sup>2</sup>	3d <sup>7</sup> 4s <sup>2</sup>	3d <sup>10</sup> 4s <sup>2</sup>
	M <sup>+</sup>	3d <sup>1</sup> 4s <sup>1</sup>	3d <sup>2</sup> 4s <sup>1</sup>	3d <sup>3</sup> 4s <sup>1</sup>	3d <sup>5</sup>	3d <sup>5</sup> 4s <sup>1</sup>	3d <sup>6</sup> 4s <sup>1</sup>	3d <sup>7</sup> 4s <sup>1</sup>	3d <sup>8</sup> 4s <sup>1</sup>
	M <sup>2+</sup>	3d <sup>1</sup>	3d <sup>2</sup>	3d <sup>3</sup>	3d <sup>1</sup>	3d <sup>5</sup>	3d <sup>6</sup>	3d <sup>7</sup>	3d <sup>8</sup>
	M <sup>3+</sup>	[Ar]	3d <sup>1</sup>	3d <sup>2</sup>	3d <sup>3</sup>	3d <sup>1</sup>	3d <sup>5</sup>	3d <sup>6</sup>	3d <sup>7</sup>
Enthalpy of atomization $\Delta_1 H^\ominus / \text{kJ mol}^{-1}$		326	473	515	397	281	416	425	430
Ionisation Enthalpy, $\Delta_1 H^\ominus / \text{kJ mol}^{-1}$	I	631	656	650	653	717	762	758	736
$\Delta_1 H^\ominus$	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).
- (5) The maximum oxidation states of reasonable stability correspond in value to the sum of the s and d electrons upto manganese (Ti<sup>IV</sup>O<sub>2</sub>, V<sup>V</sup>O<sub>2</sub><sup>+</sup>, Cr<sup>VI</sup>O<sub>4</sub><sup>2-</sup>, Mn<sup>VII</sup>O<sub>4</sub><sup>-</sup>) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are Fe<sup>II,III</sup>, Co<sup>II,III</sup>, Ni<sup>II</sup>, Cu<sup>I,II</sup>, Zn<sup>II</sup>.
- (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., V<sup>II</sup>, V<sup>III</sup>, V<sup>IV</sup>, V<sup>V</sup>.

- (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 ).
- (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  $\text{MoO}_3$  and  $\text{WO}_3$  are not.
- (10) Low oxidation states are found when a complex compound has ligands capable of  $\pi$ -acceptor character in addition to the  $\sigma$ -bonding. For example, in  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$ , 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,  $\text{Mn}_2\text{O}_7$  is a covalent green oil. Even  $\text{CrO}_3$  and  $\text{V}_2\text{O}_5$  have low melting points. In these higher oxides, the acidic character is predominant. Thus,  $\text{Mn}_2\text{O}_7$  gives  $\text{HMnO}_4$  and  $\text{CrO}_3$  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 alkalis as well as acids to give  $\text{VO}_4^{3-}$  and  $\text{VO}_4^+$  respectively. The well characterised CrO is basic but  $\text{Cr}_2\text{O}_3$  is amphoteric.

**Oxidation state of the 1<sup>st</sup> transition series Most common ones are in bold 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		
		+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.,  $VX_2$  ( $X = Cl, Br$  or  $I$ )

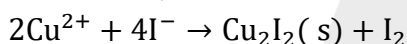
## Formulas of halides of 3d-metals

Oxidation Number									
+6			$CrF_6$						
+5		$VF_5$	$CrF_5$						
+4	$TiX_4$	$VX_4^I$	$CrF_4$	$MnF_4$					
+3	$TiX_3^{III}$	$VX_3$	$CrF_3$	$MnF_3$	$FeX_3^I$	$CoF_3$		$CuX_2^{II}$	$ZnX_2$
+2	$TiX_2$	$VX_2$	$CrF_2$	$MnX_2$	$FeX_2$	$CoX$	$NiX_2$	$CuX^{III}$	
+1									

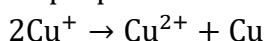
Key :  $X = F \rightarrow I$ ;  $X^I = F \rightarrow Br$ ;  $X^{II} = F \rightarrow Cl$ ;  $X^{III} = Cl \rightarrow I$

and the same applies to  $CuX$ . On the other hand, all  $Cu(II)$  halides are known except the iodide.

In this case,  $Cu^{2+}$  oxidises  $I^-$  to  $I_2$  :



(5) However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.



(6) The stability of  $Cu^{2+}(aq)$  rather than  $Cu^+(aq)$  is due to the much more negative  $\Delta_{Hyd}H^\circ$  of  $Cu^{2+}(aq)$  than  $Cu^+$ , 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  $Sc_2O_3$  to  $Mn_2O_7$ .

(9) Beyond Group 7, no higher oxides of  $Fe$  above  $Fe_2O_3$ , are known, although ferrates (VI)  $(FeO_4)^{2-}$ , are formed in alkaline media but they readily decompose to  $Fe_2O_3$  and  $O_2$ .

(10) Besides the oxides, oxocations stabilise  $V^V$  as  $VO_2^+$ ,  $V^{IV}$  as  $VO^{2+}$  and  $Ti^{IV}$  as  $TiO^{2+}$

(11) The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. Thus the highest  $Mn$  fluoride is  $MnF_4$  whereas the highest oxide is  $Mn_2O_7$ . The ability of oxygen to form multiple bonds to metals explains its superiority.

(12) In the covalent oxide  $Mn_2O_7$ , each  $Mn$  is tetrahedrally surrounded by  $O$  's including a  $Mn-O-Mn$  bridge.

(13) The tetrahedral  $[MO_4]^n$  ions are known for  $V^V$ ,  $Cr^{VI}$ ,  $Mn^V$ ,  $Mn^{VI}$  and  $Mn^{VII}$ . FORMATION OF COLOURED ION:

## Colour: (aquated)

$Ta^{4+} \rightarrow$  colourless

$V^{4+} \rightarrow$  blue

$V^{2+} \rightarrow$  violet

$Cr^{3+} \rightarrow$  green

$Mn^{2+} \rightarrow$  light pink

$Fe^{3+} \rightarrow$  yellow

$Ni^{2+} \rightarrow$  green

$Sc^{3+} \rightarrow$  colourless

$Ti^{3+} \rightarrow$  purple

$V^{3+} \rightarrow$  green

$Cr^{2+} \rightarrow$  blue

$Mn^{3+} \rightarrow$  violet

$Fe^{2+} \rightarrow$  light green

$Co^{2+} \rightarrow$  pink

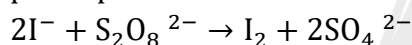
$\text{Zn}^{2+} \rightarrow$  colourless $\text{Cu}^{2+} \rightarrow$  blue**CATALYTIC PROPERTIES**

(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.

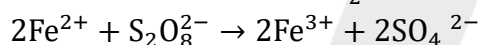
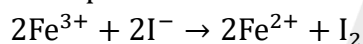
(2) Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3 d and 4 s electrons for bonding).

(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).

(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:



Catalyst	Used
$\text{TiCl}_3 \rightarrow$	Used as the Ziegler-Natta catalyst in the production of polythene.
$\text{V}_2\text{O}_5 \rightarrow$	Convert $\text{SO}_2$ to $\text{SO}_3$ in the contact process for making $\text{H}_2\text{SO}_4$
$\text{MnO}_2 \rightarrow$	Used as a catalyst to decompose $\text{KClO}_3$ to give $\text{O}_2$
$\text{Fe} \rightarrow$	Promoted iron is used in the Haber-Bosch process for making $\text{NH}_3$
$\text{FeCl}_3 \rightarrow$	Used in the production of $\text{CCl}_4$ from $\text{CS}_2$ and $\text{Cl}_2$
$\text{PdCl}_2 \rightarrow$	Wacker process for converting $\text{C}_2\text{H}_4 + \text{H}_2\text{O} + \text{PdCl}_2$ to $\text{CH}_3\text{CHO} + 2\text{HCl} + \text{Pd}$ .
$\text{Pd} \rightarrow$	Used for hydrogenation (e.g. phenol to cyclohexanone).
$\text{Pt/PtO} \rightarrow$	Adams catalyst, used for reductions.
$\text{Pt} \rightarrow$	Formerly used for $\text{SO}_2 \rightarrow \text{SO}_3$ in the contact process for making $\text{H}_2\text{SO}_4$
$\text{Pt/Rh} \rightarrow$	Formerly used in the Ostwald process for making $\text{HNO}_3$ to oxidize $\text{NH}_3$ to $\text{NO}$
$\text{Cu} \rightarrow$	Is used in the direct process for manufacture of $(\text{CH}_3)_2\text{SiCl}_2$ used to make silicones.
$\text{Cu/V} \rightarrow$	Oxidation of cyclohexanol/cyclohexanone mixture to adipic acid which is used to make nylon-66
$\text{CuCl}_2 \rightarrow$	Deacon process of making $\text{Cl}_2$ from $\text{HCl}$
$\text{Ni} \rightarrow$	Raney nickel, numerous reduction processes (e.g. manufacture of hexamethylenediamine, production of $\text{H}_2$ from $\text{NH}_3$ , reducing anthraquinone to anthraquinol in the production of $\text{H}_2\text{O}_2$ )

**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.

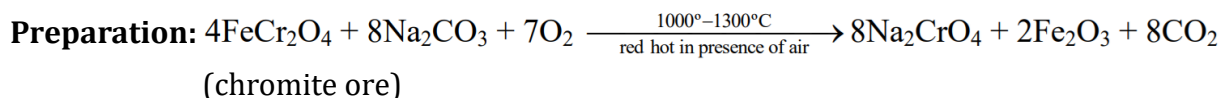
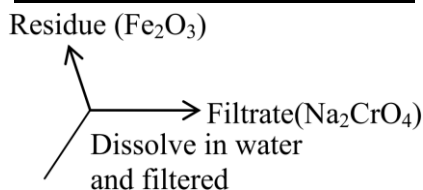
**Alloy Formation**

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.

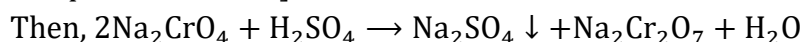
Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of 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.

**Do yourself -1**

1. Addition of non-metals like B and C to the interstitial sites of a transition metal results the metal  
(A) of more ductability (B) of less ductability  
(C) less malleable (D) of more hardness
2. The ionisation energies of transition elements are  
(A) less than p-block elements (B) more than s-block elements  
(C) less than s-block elements (D) more than p-block elements
3. Transition elements having more tendency to form complex than representative elements (s and p-block elements) due to  
(A) availability of d-orbitals for bonding  
(B) variable oxidation states are not shown by transition elements  
(C) all electrons are paired in d-orbitals  
(D) f-orbitals are available for bonding
4. The metal(s) which does/do not form amalgam is/are  
(A) Fe (B) Pt (C) Zn (D) Ag
5. Transition elements are usually characterised by variable oxidation states but Zn does not show this property because of  
(A) completion of np-orbitals (B) completion of  $(n - 1)d$  orbitals  
(C) completion of ns-orbitals (D) inert pair effect

**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]

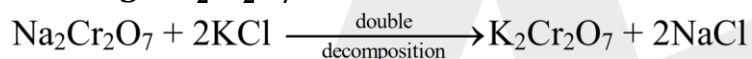


Its solubility  
 Conc. Upto  $32^\circ\text{C}$  increases  
 And then decreases

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)

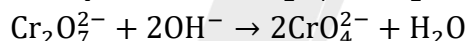
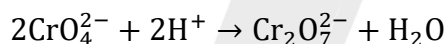
**How to get  $\text{K}_2\text{Cr}_2\text{O}_7$  :**



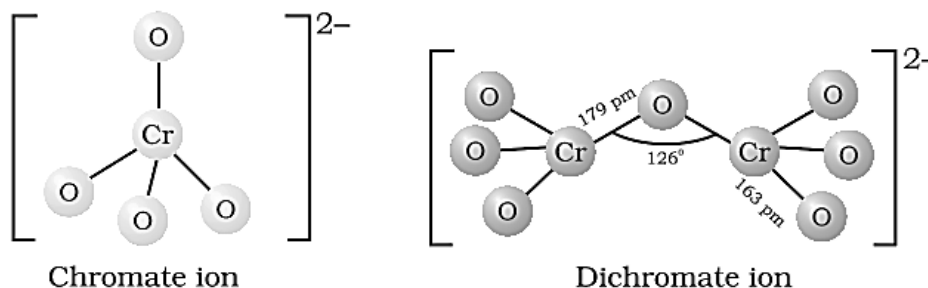
Hot conc.

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

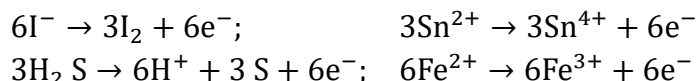
**The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.**



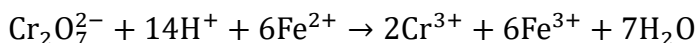
The structures of chromate ion,  $\text{CrO}_4^{2-}$  and the dichromate ion,  $\text{Cr}_2\text{O}_7^{2-}$  are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with  $\text{Cr}-\text{O}-\text{Cr}$  bond angle of  $126^\circ$ . Sodium 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:



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:

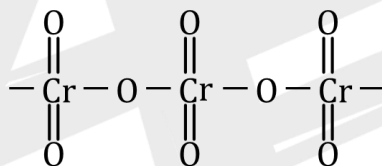


The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, for e.g.,



Similarities between hexavalent Cr & S-compounds:

- (i)  $\text{SO}_3$  &  $\text{CrO}_3 \rightarrow$  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
- (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



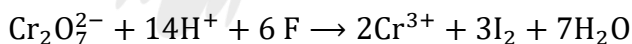
**Q. In laboratory  $\text{K}_2\text{Cr}_2\text{O}_7$  is used mainly not  $\text{Na}_2\text{Cr}_2\text{O}_7$ . Why?**

**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.

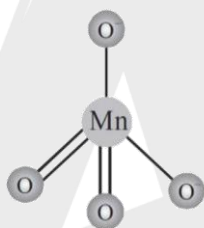
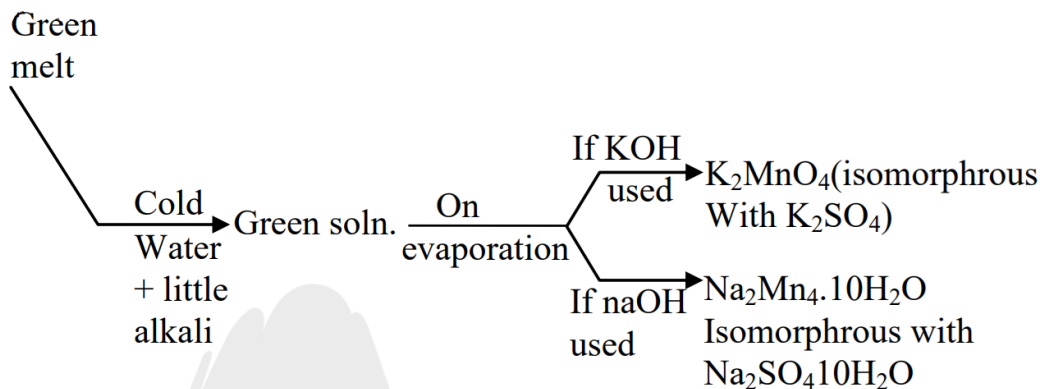
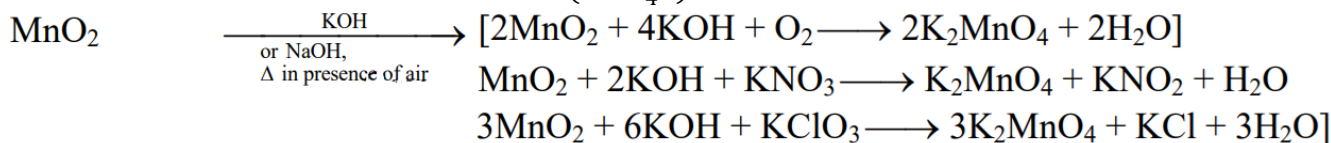
**Q. How to standardise  $\text{Na}_2\text{S}_2\text{O}_3$  solution in iodometry?**

**Sol.**  $\text{K}_2\text{Cr}_2\text{O}_7$  is primary standard  $\Rightarrow$  strength is known by weighing the salt in chemical balance and dissolving in measured amount of water.

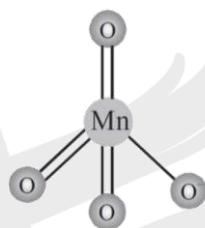
Then in acidic solution add. KI



This  $\text{I}_2$  is liberated can be estimated with  $\text{S}_2\text{O}_3^{2-}$ .

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

Tetrahedral manganate (green) ion



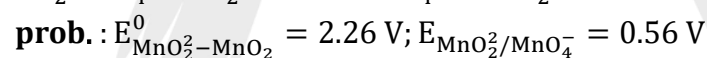
Tetrahedral permanganate (purple) ion

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.

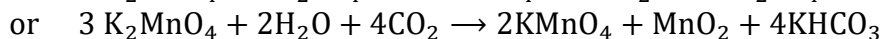
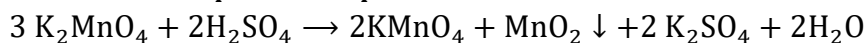
Manganate is also obtained when  $\text{KMnO}_4$  is boiled with  $\text{KOH}$ .



**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.



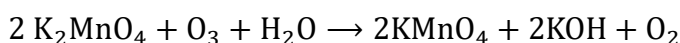
Prove that  $\text{MnO}_4^{2-}$  will disproportionate in acidic medium.

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

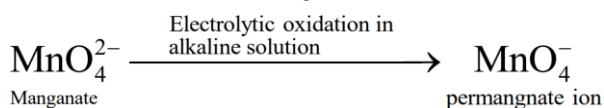
But in the above method  $\frac{1}{3}$  of Mn is lost as  $\text{MnO}_2$  but when oxidised either by  $\text{Cl}_2$  or by  $\text{O}_3$

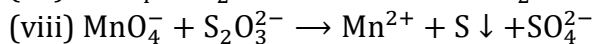
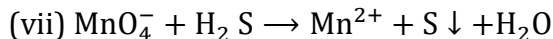
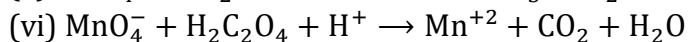
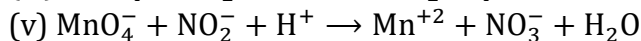
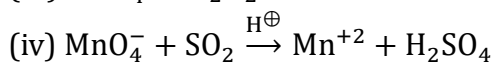
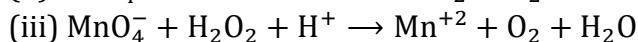
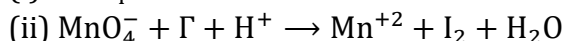
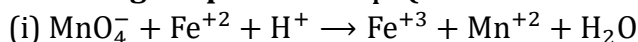


OR



OR



**Oxidising Prop. of  $\text{KMnO}_4$  : (in acidic medium)**

(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  $\text{MnO}_2$ .

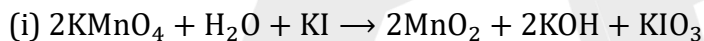
(2) It is slowly reduced to  $\text{MnO}_2$  especially in presence of light or acid



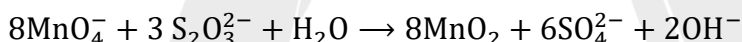
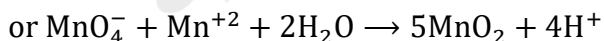
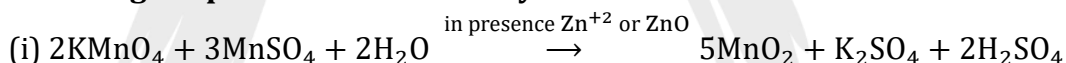
Hence it should be kept in dark bottles and standardise just before use.



**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.**

(iv) Thiosulphate is oxidised almost quantitatively to sulphate:

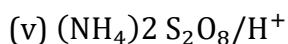
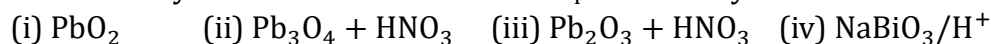
**Oxidising Prop. in neutral or weakly acidic solution:**

In absence of  $\text{Zn}^{+2}$  ions, some of the  $\text{Mn}^{+2}$  ion may escape, oxidation through the formation of insoluble  $\text{Mn}^{\text{II}}[\text{Mn}^{\text{IV}}\text{O}_3]$  manganous permanganite.

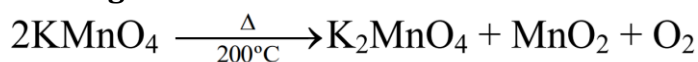
**Uses of  $\text{KMnO}_4$ :**

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.

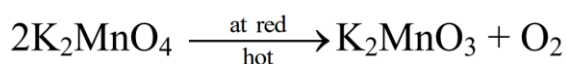
In laboratory conversion of  $\text{Mn}^{+2}$  to  $\text{MnO}_4^-$  is done by :



Heating effect:

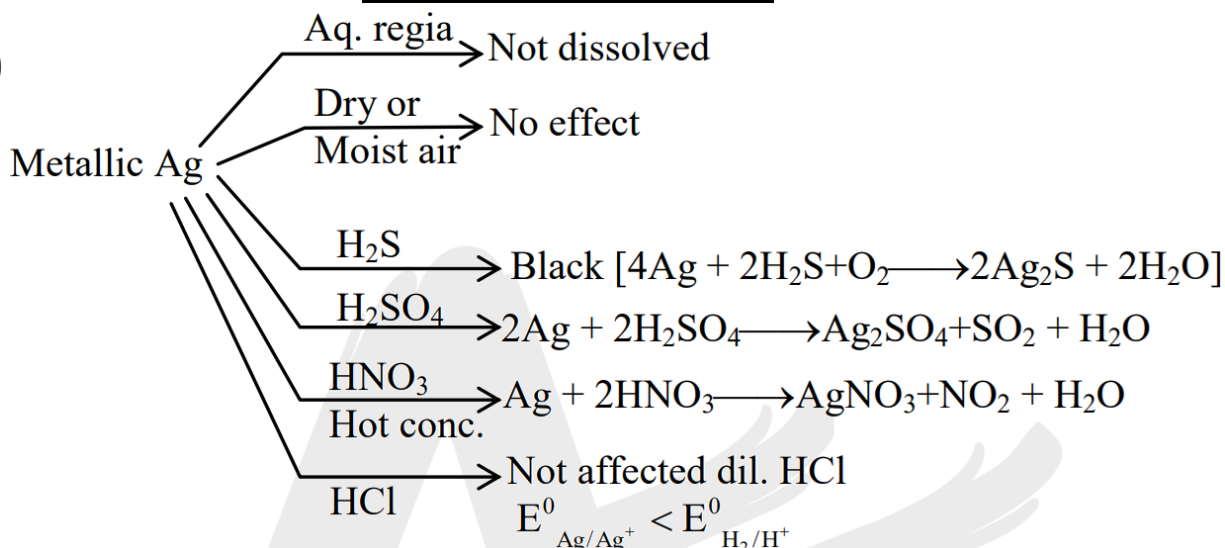


green                      Black



**SILVER AND ITS COMPOUND**

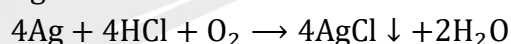
(I)



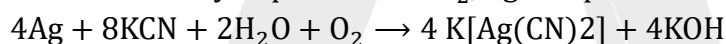
$$E^0_{\text{Ag}/\text{Ag}^+} < E^0_{\text{H}_2/\text{H}^+}$$

Hence in presence of O<sub>2</sub>.

Ag reacts with dil. HCl



In the same way in presence of O<sub>2</sub>, Ag complexes with NaCN/KCN.



AgNO<sub>3</sub>

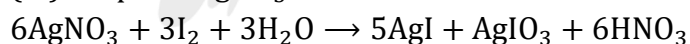
**Preparation:** Reaction of Ag with dilute HNO<sub>3</sub> or conc. HNO<sub>3</sub>.

**Properties:**

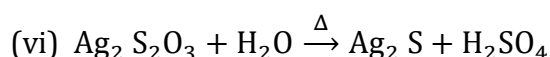
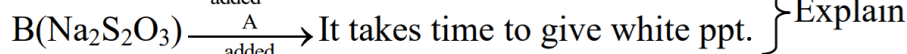
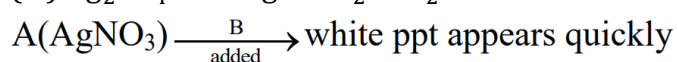
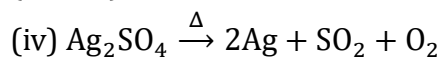
(i) It is called as lunar caustic because in contact with skin it produces burning sensation like that of caustic soda with the formation of finely divided silver (black colour)

(ii) Thermal decomposition :

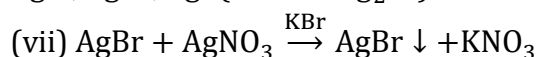
(iii) Props. of AgNO<sub>3</sub>



(excess)

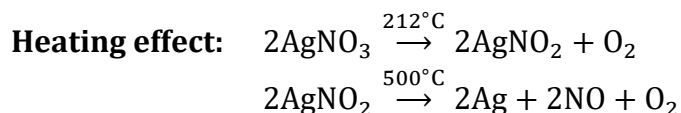


AgCl, AgBr, AgI (but not Ag<sub>2</sub>S) are soluble in Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> forming [Ag(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]<sup>-3</sup> complexes

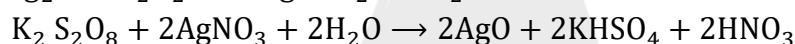
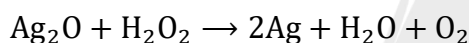
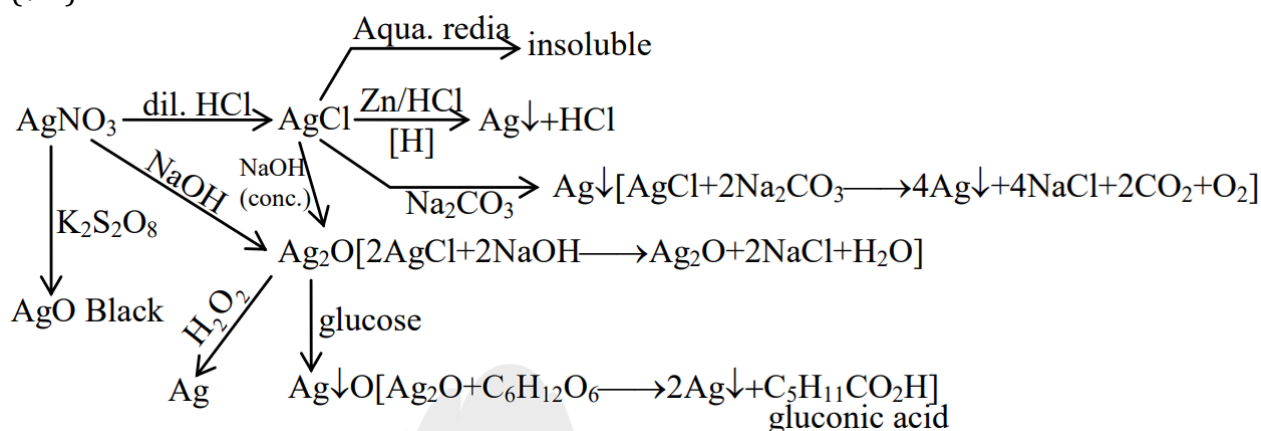


Pale yellow

ppt.

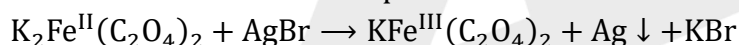


(viii)



$\text{AgO}$  supposed to be paramagnetic due to  $d^9$  configuration. But actually it is diamagnetic and exists as  $\text{Ag}^I[\text{Ag}^{III}\text{O}_2]$

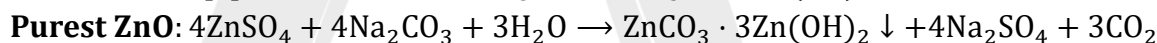
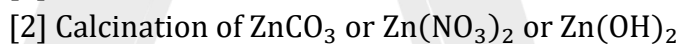
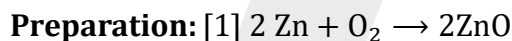
Reaction involved in developer :



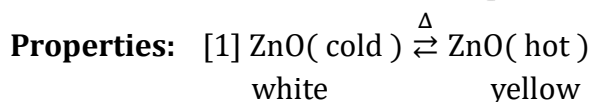
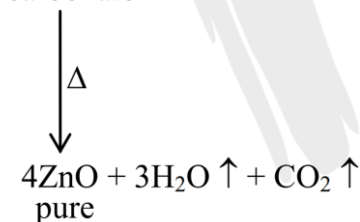
### ZINC COMPOUNDS

#### **ZnO**

It is called as phillospher's wool due to its wooly flock type appearance



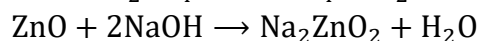
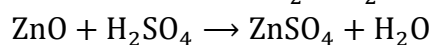
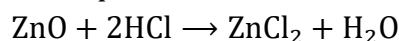
White basic zinc carbonate

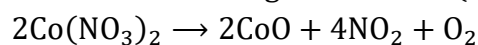
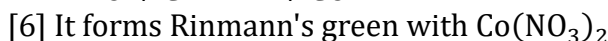
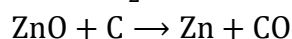
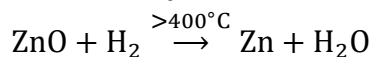
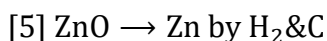


[2] It is insoluble in water

[3] It sublimes at  $400^\circ\text{C}$

[4] It is amphoteric oxide, react with acid & base both.





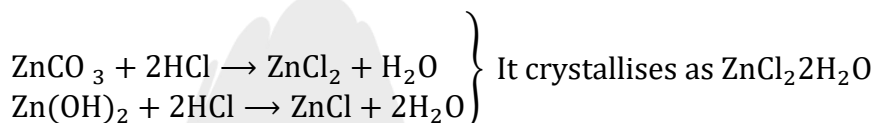
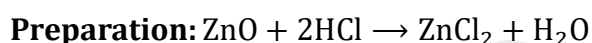
Rinmann's green

**Uses:** (1) As white pigment, it is superior than white lead because it does not turn into black

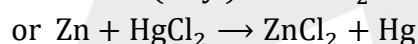
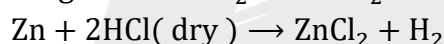
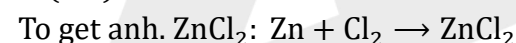
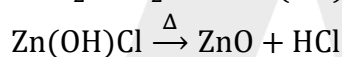
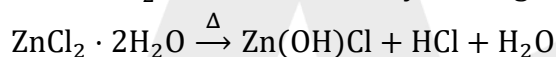
(2) Rinmann's green is used as green pigment

(3) It is used as zinc ointment in medicine

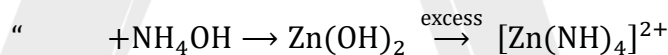
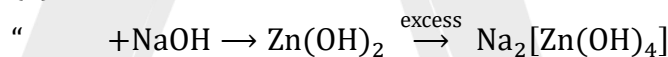
### ZnCl<sub>2</sub>



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)

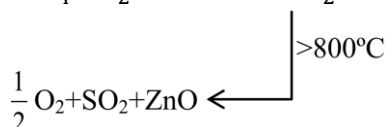
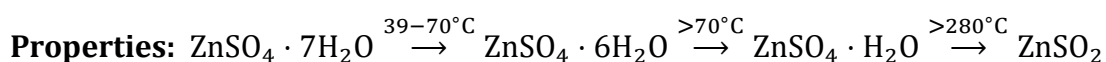
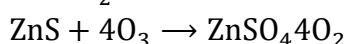
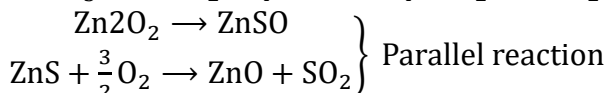
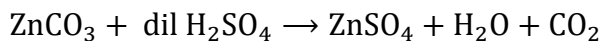
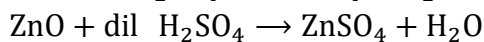
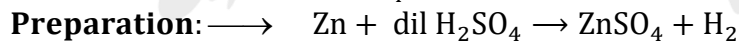


**Uses:** [1] Used for impregnating timber to prevent destruction by insects

[2] As dehydrating agent when anhydrous

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

### ZnSO<sub>4</sub>



**Uses:** [1] in eye lotion

[2] Lithophone making ( $\text{ZnS} + \text{BaSO}_4$ ) as white pigment

### COPPER COMPOUNDS

#### **CuO**

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

Malachite Green

(native Cu-carbonate)

(ii)  $2\text{Cu} + \text{O}_2 \rightarrow 2\text{CuO}$  &  $\text{Cu}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CuO}$

(iii)  $\text{Cu(OH)}_2 \xrightarrow{\Delta} \text{CuO} + \text{H}_2\text{O}$

(iv)  $2\text{Cu(NO}_3)_2 \xrightarrow{250^\circ\text{C}} 2\text{CuO} + 4\text{NO}_2 + \text{O}_2$

**Properties:** (i) CuO is insoluble in water

(ii) Readily dissolves in dil. Acids

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

$\text{HCl} \rightarrow \text{CuCl}_2$

$\text{HNO}_3 \rightarrow \text{Cu(NO}_3)_2$

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

$4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2$

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

$\text{CuO} + \text{C} \rightarrow \text{Cu} + \text{CO} \uparrow$

$\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O} \uparrow$

#### **CuCl<sub>2</sub>**

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

$\text{Cu(OH)}_2 \cdot \text{CuCO}_3 + 4\text{HCl} \rightarrow 2\text{CuCl}_2 + 3\text{H}_2\text{O} + \text{CO}_2$

**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  $[\text{Cu(H}_2\text{O)}_4]^{2+}$  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  $2[\text{Cu(H}_2\text{O)}_4]\text{Cl}_2 \rightleftharpoons [\text{Cu(H}_2\text{O)}_4]^{2+} + [\text{CuCl}_4]^{2-} + 4\text{H}_2\text{O}$

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

(a)  $\text{CuCl}_2 + \text{Cu-turnings} \xrightarrow{\Delta} 2\text{CuCl}$

(b)  $2\text{CuCl}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow 2\text{CuCl} + 2\text{HCl} + 2\text{H}_2\text{SO}_4$

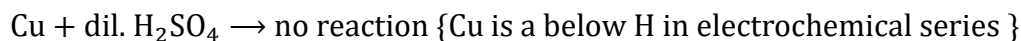
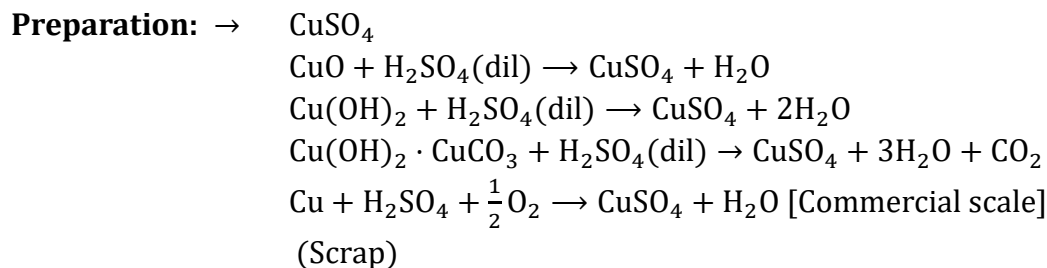
(c)  $2\text{CuCl}_2 + \text{Zn/HCl} \rightarrow 2\text{CuCl} + \text{ZnCl}_2$

(d)  $\text{CuCl}_2 + \text{SnCl}_2 \rightarrow \text{CuCl} + \text{SnCl}_4$

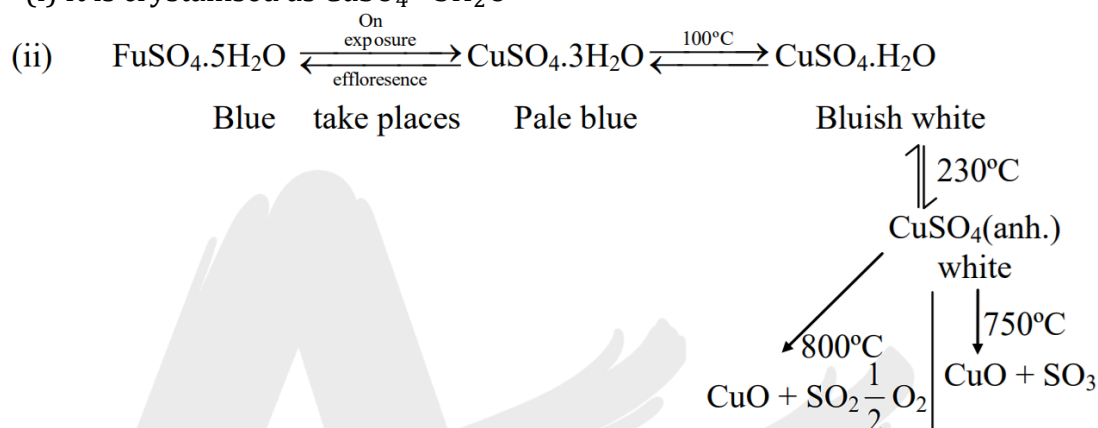
$\text{CuF}_3 \cdot 2\text{H}_2\text{O} \rightarrow \text{light blue}$   
 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{green}$   
 $\text{CuBr}_2 \rightarrow \text{almost black}$

Anh.  $\text{CuCl}_2$  is dark brown mass obtained  
 By heating  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  at  $150^\circ\text{C}$  in presence  
 of HCl vap.

$\text{CuI}_2$  does not exist  
 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} \xrightarrow[150^\circ\text{C}]{\text{HCl gas}} \text{CuCl}_2 + 2\text{H}_2\text{O}$

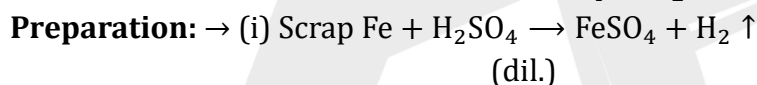
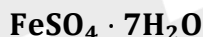


**Properties:**  $\rightarrow$  (i) It is crystallised as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

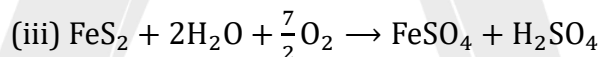
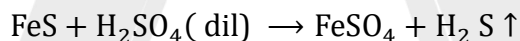


(iii) Revision with all others reagent

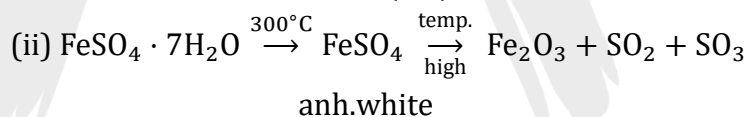
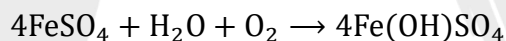
### IRON COMPOUNDS



(ii) From Kipp's waste



**Properties:**  $\rightarrow$  (i) It undergoes aerial oxidation forming basic ferric sulphate

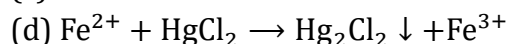
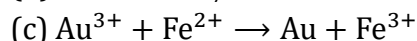
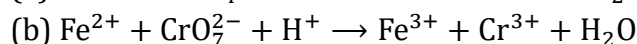
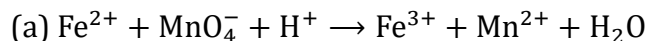


(iii) Aq. solution is acidic due to hydrolysis



weak base

(iv) It is a reducing agent



white ppt.

(v) It forms double salt. Example  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$

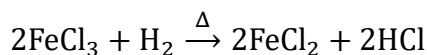
**FeO(Black)**

**Preparation:**  $\text{FeC}_2\text{O}_4 \xrightarrow[\text{in absence of air}]{\Delta} \text{FeO} + \text{CO} + \text{CO}_2$

**Properties:** It is stable at high temperature and on cooling slowly disproportionates into  $\text{Fe}_3\text{O}_4$  and iron  
 $4\text{FeO} \rightarrow \text{Fe}_3\text{O}_4 + \text{Fe}$

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

**Preparation:**  $\text{Fe} + 2\text{HCl} \xrightarrow[\text{a current of HCl}]{\text{heated in}} \text{FeCl}_2 + \text{H}_2$

**OR**

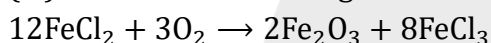
**Properties:** → (i) It is deliquescent in air like  $\text{FeCl}_3$

(ii) It is soluble in water, alcohol and ether also because it is suffi Covalent in nature

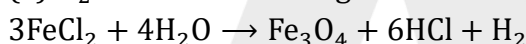
(iii) It volatilises at about  $1000^\circ\text{C}$  and vapour density indicates the presen of  $\text{Fe}_2\text{Cl}_4$ .

Above  $1300^\circ\text{C}$  density becomes normal

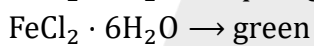
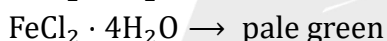
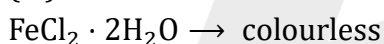
(iv) It oxidises on heating in air



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



(vi) It can exist as different hydrated form

**DO YOURSELF - 2**

- $\text{Cr}_2\text{O}_7^{2-} \xrightleftharpoons[\text{Y}]{\text{X}} 2\text{CrO}_4^{2-}$ , X and Y are respectively

(A)  $\text{X} = \text{OH}^-$ ,  $\text{Y} = \text{H}^+$  (B)  $\text{X} = \text{H}^+$ ,  $\text{Y} = \text{OH}^-$

(C)  $\text{X} = \text{OH}^-$ ,  $\text{Y} = \text{H}_2\text{O}_2$  (D)  $\text{X} = \text{H}_2\text{O}_2$ ,  $\text{Y} = \text{OH}^-$
- Acidified chromic acid +  $\text{H}_2\text{O}_2 \xrightarrow{\text{Org. solvent}} \text{X} + \text{Y}$ , X and Y are (blue colour)

(A)  $\text{CrO}_5$  and  $\text{H}_2\text{O}$  (B)  $\text{Cr}_2\text{O}_3$  and  $\text{H}_2\text{O}$

(C)  $\text{CrO}_2$  and  $\text{H}_2\text{O}$  (D)  $\text{CrO}$  and  $\text{H}_2\text{O}$
- $\text{Cu} + \text{conc. HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + \text{X}$  (oxide of nitrogen); then X is (hot)

(A)  $\text{N}_2\text{O}$  (B)  $\text{NO}_2$  (C)  $\text{NO}$  (D)  $\text{N}_2\text{O}_3$
- $\text{CuSO}_4$  solution reacts with excess KCN to give

(A)  $\text{Cu}(\text{CN})_2$  (B)  $\text{CuCN}$  (C)  $\text{K}_2[\text{Cu}(\text{CN})_2]$  (D)  $\text{K}_3[\text{Cu}(\text{CN})_4]$
- In the equation:  $\text{M} + 8\text{CN}^- + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4[\text{M}(\text{CN})_2]^- + 4\text{OH}^-$ , metal M is

(A) Ag (B) Au (C) Cu (D) Hg

## EXERCISE-I

Select one or more than one correct options.

Q.1 (T) imparts violet colour in the flame test  $\xrightarrow{\text{compd (U) + conc. H}_2\text{SO}_4}$  (V) Red gas  $\xrightarrow{\text{NaOH} + \text{AgNO}_3}$

(W) Red ppt.  $\xrightarrow{\text{NH}_3 \text{ soln.}}$  (X)

(W) Red ppt.  $\xrightarrow{\text{dil HCl}}$  (Y) white ppt.

(U)  $\xrightarrow[\text{NaOH}]{\Delta}$  (Z) gas (gives white fumes with HCl)

sublimes on heating

Identify (T) to (Z).

(A) T =  $\text{KMnO}_4$ , U = HCl, V =  $\text{Cl}_2$ , W =  $\text{HgI}_2$ , X =  $\text{Hg}(\text{NH}_2)\text{NO}_3$ , Y =  $\text{Hg}_2\text{Cl}_2$ , Z =  $\text{N}_2$

(B) T =  $\text{K}_2\text{Cr}_2\text{O}_7$ , U =  $\text{NH}_4\text{Cl}$ , V =  $\text{CrO}_2\text{Cl}_2$ , W =  $\text{Ag}_2\text{CrO}_4$ , X =  $[\text{Ag}(\text{NH}_3)_2]^+$ , Y = AgCl, Z =  $\text{NH}_3$

(C) T =  $\text{K}_2\text{CrO}_4$ , U = KCl, V =  $\text{CrO}_2\text{Cl}_2$ , W =  $\text{HgI}_2$ , X =  $\text{Na}_2\text{CrO}_4$ , Y =  $\text{BaCO}_3$ , Z =  $\text{NH}_4\text{Cl}$

(D) T =  $\text{K}_2\text{MnO}_4$ , U = NaCl, V =  $\text{CrO}_3$ , W =  $\text{AgNO}_2$ , X =  $(\text{NH}_4)_2\text{CrO}_4$ , Y =  $\text{CaCO}_3$ , Z =  $\text{SO}_2$

Q.2 The number of moles of acidified  $\text{KMnO}_4$  required to convert one mole of sulphite ion into sulphate ion is

(A) 2/5

(B) 3/5

(C) 4/5

(D) 1

Q.3  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \xrightleftharpoons{\text{Fe+Mo}} 2\text{NH}_3(\text{g})$ ; Haber's process, Mo is used as

(A) a catalyst

(B) a catalytic promoter

(C) an oxidising agent

(D) as a catalytic poison

Q.4 Potash alum is a double salt, its aqueous solution shows the characteristics of

(A)  $\text{Al}^{3+}$  ions

(B)  $\text{K}^+$  ions

(C)  $\text{SO}_4^{2-}$  ions

(D)  $\text{Al}^{3+}$  ions but not  $\text{K}^+$  ions

Q.5 Mercury is a liquid at  $0^\circ\text{C}$  because of

(A) very high ionisation energy

(B) weak metallic bonds

(C) high heat of hydration

(D) high heat of sublimation

Q.6  $\text{CrO}_3$  dissolves in aqueous NaOH to give

(A)  $\text{Cr}_2\text{O}_7^{2-}$

(B)  $\text{CrO}_4^{2-}$

(C)  $\text{Cr}(\text{OH})_3$

(D)  $\text{Cr}(\text{OH})_2$

Q.7 The correct statement(s) about transition elements is/are

(A) the most stable oxidation state is +3 and its stability decreases across the period

(B) transition elements of 3 d-series have almost same atomic sizes from Cr to Cu

(C) the stability of +2 oxidation state increases across the period

(D) some transition elements like Ni, Fe, Cr may show zero oxidation state in some of their compounds

## (Organic Chemistry)

## d-BLOCK ELEMENTS

- Q.8** An ornamental of gold having 75% of gold, it is of carat.  
 (A) 18 (B) 16 (C) 24 (D) 20
- Q.9** Solution of  $\text{MnO}_4^-$  is purple-coloured due to  
 (A) d-d-transition  
 (B) charge transfer from O to Mn  
 (C) due to both d-d-transition and charge transfer  
 (D) none of these
- Q.10** During estimation of oxalic acid Vs  $\text{KMnO}_4$ , self indicator is  
 (A)  $\text{KMnO}_4$  (B) oxalic acid (C)  $\text{K}_2\text{SO}_4$  (D)  $\text{MnSO}_4$
- Q.11** Which of the following statements concern with transition metals?  
 (A) compounds containing ions of transition elements are usually coloured  
 (B) Zinc has lowest melting point among 3d-series elements  
 (C) they show variable oxidation states, which differ by two units only  
 (D) they easily form complexes
- Q.12** Correct statement(s) is/are  
 (A) an acidified solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  liberates iodine from KI  
 (B)  $\text{K}_2\text{Cr}_2\text{O}_7$  is used as a standard solution for estimation of  $\text{Fe}^{2+}$  ions  
 (C) in acidic medium,  $M = N/6$  for  $\text{K}_2\text{Cr}_2\text{O}_7$   
 (D)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  on heating decomposes to yield  $\text{Cr}_2\text{O}_3$  through an endothermic reaction
- Q.13** The highest oxidation state among transition elements is  
 (A) +7 by Mn (B) +8 by Os (C) +8 by Ru (D) +7 by Fe
- Q.14** A compound of mercury used in cosmetics, in Ayurvedic and Yunani medicines and known as Vermilion is  
 (A)  $\text{HgCl}_2$  (B)  $\text{HgS}$  (C)  $\text{Hg}_2\text{Cl}_2$  (D)  $\text{HgI}$
- Q.15**  $\uparrow \text{Y(g)} \xleftarrow{\text{KI}} \text{CuSO}_4 \xrightarrow{\text{dil. SO}_4} \text{X (Blue colour)}$ , X and Y are  
 (A)  $\text{X} = \text{I}_2$ ,  $\text{Y} = [\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  (B)  $\text{X} = [\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ,  $\text{Y} = \text{I}_2$   
 (C)  $\text{X} = [\text{Cu}(\text{H}_2\text{O})_4]^+$ ,  $\text{Y} = \text{I}_2$  (D)  $\text{X} = [\text{Cu}(\text{H}_2\text{O})_5]^{2+}$ ,  $\text{Y} = \text{I}_2$
- Q.16**  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  (Ammonium dichromate) is used in fireworks. The green coloured powder blown in air is  
 (A)  $\text{Cr}_2\text{O}_3$  (B)  $\text{CrO}_2$  (C)  $\text{Cr}_2\text{O}_4$  (D)  $\text{CrO}_3$
- Q.17** The d-block element which is a liquid at room temperature, having high specific heat, less reactivity than hydrogen and its chloride ( $\text{MX}_2$ ) is volatile on heating is  
 (A) Cu (B) Hg (C) Ce (D) Pm

## (Organic Chemistry)

## d-BLOCK ELEMENTS

- Q.18** Coinage metals show the properties of  
 (A) typical elements (B) normal elements  
 (C) inner-transition elements (D) transition element
- Q.19** Iron becomes passive by..... due to formation of.....  
 (A) dil. HCl,  $\text{Fe}_2\text{O}_3$  (B) 80% conc.  $\text{HNO}_3$ ,  $\text{Fe}_3\text{O}_4$   
 (C) conc.  $\text{H}_2\text{SO}_4$ ,  $\text{Fe}_3\text{O}_4$  (D) conc. HCl,  $\text{Fe}_3\text{O}_4$
- Q.20** Bayer's reagent used to detect olefinic double bond is  
 (A) acidified  $\text{KMnO}_4$  (B) aqueous  $\text{KMnO}_4$   
 (C) 1% alkaline  $\text{KMnO}_4$  solution (D)  $\text{KMnO}_4$  in benzene
- Q.21** Amphoteric oxide(s) is/are  
 (A)  $\text{Al}_2\text{O}_3$  (B)  $\text{SnO}$  (C)  $\text{ZnO}$  (D)  $\text{Fe}_2\text{O}_3$
- Q.22** Interstitial compounds are formed by  
 (A) Co (B) Ni (C) Fe (D) Ca
- Q.23** The transition metal used in X-rays tube is  
 (A) Mo (B) Ta (C) Tc (D) Pm
- Q.24** The catalytic activity of transition elements is related to their  
 (A) variable oxidation states (B) surface area  
 (C) complex formation ability (D) magnetic moment
- Q.25**  $\text{MnO}_4^- + x\text{e}^- \xrightarrow{\text{(Alkaline medium)}} \text{MnO}_4^{2-}$   
 $\quad \quad \quad + y\text{e}^- \xrightarrow{\text{(Acidic medium)}} \text{Mn}^{2+}$   
 $\quad \quad \quad + z\text{e}^- \xrightarrow{\text{(Neutral medium)}} \text{MnO}_2$   
 x, y and z are respectively  
 (A) 1,2,3 (B) 1,5,3 (C) 1,3,5 (D) 5,3,1
- Q.26** When  $\text{KMnO}_4$  solution is added to hot oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time. This is because  
 (A)  $\text{Mn}^{2+}$  acts as auto catalyst (B)  $\text{CO}_2$  is formed  
 (C) Reaction is exothermic (D)  $\text{MnO}_4^-$  catalyses the reaction.
- Q.27** The higher oxidation states of transition elements are found to be in the combination with A and B, which are  
 (A) F, O (B) O, N (C) O, Cl (D) F, Cl

- Q.28** An element of 3d-transition series shows two oxidation states  $x$  and  $y$ , differ by two units then  
(A) compounds in oxidation state  $x$  are ionic if  $x > y$   
(B) compounds in oxidation state  $x$  are ionic if  $x < y$   
(C) compounds in oxidation state  $y$  are covalent if  $x < y$   
(D) compounds in oxidation state  $y$  are covalent if  $y < x$
- Q.29** Pick out the incorrect statement:  
(A)  $\text{MnO}_2$  dissolves in conc.  $\text{HCl}$ , but does not form  $\text{Mn}^{4+}$  ions  
(B)  $\text{MnO}_2$  oxidizes hot concentrated  $\text{H}_2\text{SO}_4$  liberating oxygen  
(C)  $\text{K}_2\text{MnO}_4$  is formed when  $\text{MnO}_2$  in fused  $\text{KOH}$  is oxidised by air,  $\text{KNO}_3$ ,  $\text{PbO}_2$  or  $\text{NaBiO}_3$   
(D) Decomposition of acidic  $\text{KMnO}_4$  is not catalysed by sunlight.
- Q.30** 1 mole of  $\text{Fe}^{2+}$  ions are oxidised to  $\text{Fe}^{3+}$  ions with the help of (in acidic medium)  
(A)  $1/5$  moles of  $\text{KMnO}_4$   
(B)  $5/3$  moles of  $\text{KMnO}_4$   
(C)  $2/5$  moles of  $\text{KMnO}_4$   
(D)  $5/2$  moles of  $\text{KMnO}_4$
- Q.31** The metals present in insulin and haemoglobin are respectively  
(A)  $\text{Zn}$ ,  $\text{Hg}$  (B)  $\text{Zn}$ ,  $\text{Fe}$  (C)  $\text{Co}$ ,  $\text{Fe}$  (D)  $\text{Mg}$ ,  $\text{Fe}$
- Q.32** To an acidified dichromate solution, a pinch of  $\text{Na}_2\text{O}_2$  is added and shaken. What is observed:  
(A) blue colour (B) Orange colour changing to green  
(C) Copious evolution of oxygen (D) Bluish - green precipitate
- Q.33** The rusting of iron is formulated as  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  which involves the formation of  
(A)  $\text{Fe}_2\text{O}_3$  (B)  $\text{Fe}(\text{OH})_3$  (C)  $\text{Fe}(\text{OH})_2$  (D)  $\text{Fe}_2\text{O}_3 + \text{Fe}(\text{OH})_3$
- Q.34** Metre scales are made-up of alloy  
(A) invar (B) stainless steel (C) electron (D) magnalium
- Q.35** Amongst  $\text{CuF}_2$ ,  $\text{CuCl}_2$  and  $\text{CuBr}_2$   
(A) only  $\text{CuF}_2$  is ionic  
(B) both  $\text{CuCl}_2$  and  $\text{CuBr}_2$  are covalent  
(C)  $\text{CuF}_2$  and  $\text{CuCl}_2$  are ionic but  $\text{CuBr}_2$  is covalent  
(D)  $\text{CuF}_2$ ,  $\text{CuCl}_2$  as well as  $\text{CuBr}_2$  are ionic
- Q.36** A metal  $M$  which is not affected by strong acids like conc.  $\text{HNO}_3$ , conc.  $\text{H}_2\text{SO}_4$  and conc. solution of alkalis like  $\text{NaOH}$ ,  $\text{KOH}$  forms  $\text{MCl}_3$  which finds use for toning in photography. The metal  $M$  is  
(A)  $\text{Ag}$  (B)  $\text{Hg}$  (C)  $\text{Au}$  (D)  $\text{Cu}$
- Q.37** Solid  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  having covalent, ionic as well as co-ordinate bonds. Copper atom/ion forms co-ordinate bonds with water.  
(A) 1 (B) 2 (C) 3 (D) 4

## (Organic Chemistry)

## d-BLOCK ELEMENTS

- Q.38**  $\text{CuSO}_4(\text{aq}) + 4\text{NH}_3 \rightarrow \text{X}$ , then X is  
(A)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  (B) paramagnetic  
(C) Coloured (D) of a magnetic moment of 1.73BM
- Q.39**  $\text{KMnO}_4 + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{X}(\text{g})$ , X is a (acidified)  
(A) red liquid (B) violet gas  
(C) greenish yellow gas (D) yellow-brown gas
- Q.40** Purple of Cassius is:  
(A) Pure gold (B) Colloidal solution of gold  
(C) Gold (I) hydroxide (D) Gold (III) chloride
- Q.41** Amongst the following species, maximum covalent character is exhibited by  
(A)  $\text{FeCl}_2$  (B)  $\text{ZnCl}_2$  (C)  $\text{HgCl}_2$  (D)  $\text{CdCl}_2$
- Q.42** Number of moles of  $\text{SnCl}_2$  required for the reduction of 1 mole of  $\text{K}_2\text{Cr}_2\text{O}_7$  into  $\text{Cr}_2\text{O}_3$  is (in acidic medium)  
(A) 3 (B) 2 (C) 1 (D)  $1/3$
- Q.43** Amphoteric oxide(s) of Mn is/are  
(A)  $\text{MnO}_2$  (B)  $\text{Mn}_3\text{O}_4$  (C)  $\text{Mn}_2\text{O}_7$  (D)  $\text{MnO}$
- Q.44** Pick out the incorrect statement:  
(A)  $\text{MnO}_4^{2-}$  is quite strongly oxidizing and stable only in very strong alkalies. In dilute alkali, neutral solutions, it disproportionates.  
(B) In acidic solutions,  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$  and thus,  $\text{KMnO}_4$  is widely used as oxidising agent  
(C)  $\text{KMnO}_4$  does not acts as oxidising agent in alkaline medium  
(D)  $\text{KMnO}_4$  is manufactured by the fusion of pyrolusite ore with  $\text{KOH}$  in presence of air or  $\text{KNO}_3$ , followed by electrolytic oxidation in strongly alkaline solution.
- Q.45** The aqueous solution of  $\text{CuCrO}_4$  is green because it contains  
(A) green  $\text{Cu}^{2+}$  ions (B) green  $\text{CrO}_4^{2-}$  ions  
(C) blue  $\text{Cu}^{2+}$  ions and green  $\text{CrO}_4^{2-}$  ions (D) blue  $\text{Cu}^{2+}$  ions and yellow  $\text{CrO}_4^{2-}$  ions
- Q.46** Manganese steel is used for making railway tracks because  
(A) it is hard with high percentage of Mn  
(B) it is soft with high percentage of Mn  
(C) it is hard with small concentration of manganese with impurities  
(D) it is soft with small concentration of manganese with impurities

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- Q.47** In nitroprusside ion, the iron exists as  $\text{Fe}^{2+}$  and NO as  $\text{NO}^+$  rather than  $\text{Fe}^{3+}$  and NO respectively. These forms of ions are established with the help of  
(A) Magnetic moment in solid state (B) thermal decomposition method  
(C) by reaction with KCN (D) by action with  $\text{K}_2\text{SO}_4$
- Q.48** Acidified  $\text{KMnO}_4$  can be decolourised by  
(A)  $\text{SO}_2$  (B)  $\text{H}_2\text{O}_2$  (C)  $\text{FeSO}_4$  (D)  $\text{Fe}_2(\text{SO}_4)_3$
- Q.49** Transition elements in lower oxidation states act as Lewis acid because  
(A) they form complexes (B) they are oxidising agents  
(C) they donate electrons (D) they do not show catalytic properties
- Q.50** The lanthanide contraction is responsible for the fact that  
(A) Zr and Hf have same atomic sizes (B) Zr and Hf have same properties  
(C) Zr and Hf have different atomic sizes (D) Zr and Hf have different properties
- Q.51** The Ziegler-Natta catalyst used for polymerisation of ethene and styrene is  $\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}$ , the catalysing species (active species) involved in the polymerisation is  
(A)  $\text{TiCl}_4$  (B)  $\text{TiCl}_3$  (C)  $\text{TiCl}_2$  (D)  $\text{TiCl}$
- Q.52** Ion(s) having non zero magnetic moment (spin only) is/are  
(A)  $\text{Sc}^{3+}$  (B)  $\text{Ti}^{3+}$  (C)  $\text{Cu}^{2+}$  (D)  $\text{Zn}^{2+}$
- Q.53** The electrons which take part in order to exhibit variable oxidation states by transition metals are  
(A) ns only (B)  $(n-1)d$  only  
(C) ns and  $(n-1)d$  only but not np (D)  $(n-1)d$  and np only but not ns
- Q.54** 'Bordeaux mixture' is used as a fungicide. It is a mixture of  
(A)  $\text{CaSO}_4 + \text{Cu}(\text{OH})_2$  (B)  $\text{CuSO}_4 + \text{Ca}(\text{OH})_2$   
(C)  $\text{CuSO}_4 + \text{CaO}$  (D)  $\text{CuO} + \text{CaO}$
- Q.55** Which of the following reaction is possible at anode?  
(A)  $2\text{Cr}^{3+} + 7\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+$  (B)  $\text{F}_2 \rightarrow 2\text{F}^-$   
(C)  $\frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{O}$  (D) None of these
- Q.56** Colourless solutions of the following four salts are placed separately in four different test tubes and a strip of copper is dipped in each one of these. Which solution will turn blue?  
(A)  $\text{KNO}_3$  (B)  $\text{AgNO}_3$  (C)  $\text{Zn}(\text{NO}_3)_2$  (D)  $\text{ZnSO}_4$
- Q.57** Peacock ore is:  
(A)  $\text{FeS}_2$  (B)  $\text{CuFeS}_2$  (C)  $\text{CuCO}_3$  (D)  $\text{Cu}(\text{OH})_2$

- Q.58** When acidified  $\text{KMnO}_4$  is added to hot oxalic acid solution, the decolourization is slow in the beginning, but becomes very rapid after some time. This is because:
- (A)  $\text{Mn}^{2+}$  acts as autocatalyst  
(B)  $\text{CO}_2$  is formed as the product  
(C) Reaction is exothermic  
(D)  $\text{MnO}_4^-$  catalyses the reaction

**Question No. 59 to 68**

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

- (A) if both (A) and (R) are true and (R) is the correct explanation of (A)  
(B) if both (A) and (R) are true but (R) is not correct explanation of (A)  
(C) if (A) is true but (R) is false  
(D) if (A) is false and (R) is true

- Q.59** Assertion:  $\text{KMnO}_4$  is purple in colour due to charge transfer.  
Reason: In  $\text{MnO}_4^-$ , there is no electron present in d-orbitals of manganese.
- Q.60** Assertion:  $\text{K}_2\text{CrO}_4$  has yellow colour due to charge transfer.  
Reason:  $\text{CrO}_4^{2-}$  ion is tetrahedral in shape.
- Q.61** Assertion: The highest oxidation state of chromium in its compounds is +6.  
Reason: Chromium atom has only six electrons in ns and  $(n - 1)d$  orbitals.
- Q.62** Assertion:  $\text{CrO}_3$  reacts with  $\text{HCl}$  to form chromyl chloride gas.  
Reason: Chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ) has tetrahedral shape.
- Q.63** Assertion: Zinc does not show characteristic properties of transition metals.  
Reason: In zinc outermost shell is completely filled.
- Q.64** Assertion: Tungsten has a very high melting point.  
Reason: Tungsten is a covalent compound.
- Q.65** Assertion: Equivalent mass of  $\text{KMnO}_4$  is equal to one-third of its molecular mass when it acts as an oxidising agent in an alkaline medium.  
Reason: Oxidation number of Mn is +7 in  $\text{KMnO}_4$ .
- Q.66** Assertion:  $\text{Ce}^{4+}$  is used as an oxidising agent in volumetric analysis.  
Reason:  $\text{Ce}^{4+}$  has the tendency of attain +3 oxidation state.
- Q.67** Assertion: Promethium is a man made element.  
Reason: It is radioactive and has been prepared by artificial means.
- Q.68** Assertion:  $\text{Cu}^+$  ion is colourless.  
Reason: Four water molecules are coordinated to  $\text{Cu}^+$  ion in water.

## EXERCISE-II

## JEE-MAIN

- Number of electrons transferred in each case when  $\text{KMnO}_4$  acts as an oxidising agent to give  $\text{MnO}_2$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}(\text{OH})_3$  and  $\text{MnO}_4^{2-}$  are respectively : **[AIEEE 2002, 3/225]**  
 (A) 3,5,4 and 1 (B) 4,3,1 and 5  
 (C) 1,3,4 and 5 (D) 5,4,3 and 1
- Which of the following ions has the maximum magnetic moment? **[AIEEE 2002, 3/225]**  
 (A)  $\text{Mn}^{2+}$  (B)  $\text{Fe}^{2+}$  (C)  $\text{Ti}^{2+}$  (D)  $\text{Cr}^{2+}$ .
- Most common oxidation state for Ce (Cerium) are : **[AIEEE 2002, 3/225]**  
 (A) +3, +4 (B) +2, +3 (C) +2, +4 (D) +3, +5
- 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
- Which one of the following nitrates will leave behind a metal on strong heating ? **[AIEEE 2003, 3/225]**  
 (A) Copper nitrate (B) Manganese nitrate  
 (C) Silver nitrate (D) Ferric nitrate
- 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
- 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
- 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
- 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.

10. The radius of  $\text{La}^{3+}$  (Atomic number of La = 57) is  $1.06\text{\AA}$ . Which one of the following given values will be closest to the radius of  $\text{Lu}^{3+}$  (Atomic number of Lu = 71)? [AIEEE 2003, 3/225]  
(A)  $1.60\text{\AA}$  (B)  $1.40\text{\AA}$  (C)  $1.06\text{\AA}$  (D)  $0.85\text{\AA}$
11. Cerium ( $Z = 58$ ) is an important member of the lanthanoids. Which of the following statement about cerium is incorrect? [AIEEE 2004, 3/225]  
(A) The common oxidation state of cerium are +3 and +4.  
(B) The +3 oxidation state of cerium is more stable than +4 oxidation state.  
(C) The +4 oxidation state of cerium is not known in solution.  
(D) Cerium (IV) acts as an oxidizing agent.
12. The lanthanide contraction is responsible for the fact that [AIEEE 2005, 3/225]  
(A) Zr and Y have about the same radius  
(B) Zr and Nb have similar oxidation state  
(C) Zr and Hf have about the same radius  
(D) Zr and Zn have same oxidation state.
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.
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
15. Lanthanoid contraction is caused due to: [AIEEE 2006, 3/165]  
(A) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge  
(B) the appreciable shielding on outer electrons by 5f electrons from the nuclear charge  
(C) the same effective nuclear charge from Ce to Lu  
(D) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge
16. Identify the incorrect statement among the following. [AIEEE 2007, 3/120]  
(A) The chemistry of various lanthanoids is very similar.  
(B) 4f and 5f orbitals are equally shielded.  
(C) d-block elements show irregular and erratic chemical properties among themselves.  
(D) La and Lu have partially filled d orbitals and no other partially filled orbitals.

17. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because [AIEEE 2007, 3/120]  
(A) The actinoids are more reactive than the lanthanoids.  
(B) The 5 forbitals extend farther from the nucleus than the 4 orbitals.  
(C) The 5 f orbitals are more buried than the 4 forbitals  
(D) There is a similarity between 4f and 5f orbitals in their angular part of the wave function
18. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being. [AIEEE 2008, 3/105]  
(A) lesser energy difference between 5f and 6 d than between 4f and 5 d orbitals  
(B) more energy difference between 5f and 6 d than between 4f and 5 d orbitals  
(C) more reactive nature of the actinoids than the lanthanoids  
(D) 4f orbitals more diffused than the 5 forbitals
19. In context with the transition elements, which of the following statements is incorrect? [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.
20. Knowing that the Chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statement is incorrect? [AIEEE 2009, 4/144]  
(A) The ionic sizes of Ln (III) decrease in general with increasing atomic number.  
(B) Ln (III) compounds are generally colourless.  
(C) Ln (III) hydroxides are mainly basic in character  
(D) Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character.
21. The correct order of  $E_{M^{2+}/M}^0$  values with negative sign for the four successive elements Cr, Mn, Fe and Co is [AIEEE 2010, 4/144]  
(A)  $Mn > Cr > Fe > Co$  (B)  $Cr > Fe > Mn > Co$   
(C)  $Fe > Mn > Cr > Co$  (D)  $Cr > Mn > Fe > Co$
22. In context of the lanthanoids, which of the following statement is not correct? [AIEEE 2011, 4/120]  
(A) There is a gradual decrease in the radii of the members with increasing atomic number in the series.  
(B) All the member exhibit +3 oxidation state.

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- (C) Because of similar properties the separation of lanthanoids is not easy.  
 (D) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series.

23. The outer electron configuration of Lu (Atomic No : 71) is : [AIEEE 2011, 4/120]  
 (A)  $4f^3 5d^5 6s^2$  (B)  $4f^8 5d^0 6s^2$  (C)  $4f^4 5d^4 6s^2$  (D)  $4f^{14} 5d^1 6s^2$

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  
 (C) Ferrous compounds are less volatile than the corresponding ferric compounds  
 (D) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.

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

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)

27. Which series of reactions correctly represents chemical relations related to iron and its compound? [JEE(Main) 2014, 4/120]  
 (A)  $Fe \xrightarrow{\text{dil } H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4, O_2} Fe_2(SO_4)_3 \xrightarrow{\text{heat}} Fe$   
 (B)  $Fe \xrightarrow{O_2, \text{heat}} FeO \xrightarrow{\text{dil } H_2SO_4} FeSO_4 \xrightarrow{\text{heat}} Fe$   
 (C)  $Fe \xrightarrow{Cl_2, \text{heat}} FeCl_3 \xrightarrow{\text{heat, air}} FeCl_2 \xrightarrow{Zn} Fe$   
 (D)  $Fe \xrightarrow{O_2, \text{heat}} Fe_3O_4 \xrightarrow{CO, 600^\circ C} FeO \xrightarrow{CO, 700^\circ C} Fe$

28. The equation which is balanced and represents the correct product(s) is : [JEE(Main) 2014, 4/120]  
 (A)  $Li_2O + 2KCl \rightarrow 2LiCl + K_2O$   
 (B)  $[CoCl(NH_3)_5]^+ + 5H^+ \rightarrow Co^{2+} + 5NH_4^+ + Cl^-$   
 (C)  $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{excess, NaOH}} [Mg(EDTA)]^{2-} + 6H_2O$   
 (D)  $CuSO_4 + 4KCN \rightarrow K_2[Cu(CN)_4] + K_2SO_4$

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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
30. When  $\text{XO}_2$  is fused with an alkali metal hydroxide in presence of an oxidizing agent such as  $\text{KNO}_3$ ; 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
31. The transition element that has lowest enthalpy of atomisation is : [JEE-Main 2019]  
 (A) Zn (B) Cu (C) Fe (D) V
32. Consider the following reduction processes : [JEE-Main 2019]  
 $\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn(s)}; E^\circ = -0.76 \text{ V}$   
 $\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca(s)}; E^\circ = -2.87 \text{ V}$   
 $\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg(s)}; E^\circ = -2.36 \text{ V}$   
 $\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni(s)}; E^\circ = -0.25 \text{ V}$   
 The reducing power of the metals increases in the order :  
 (A)  $\text{Ca} < \text{Mg} < \text{Zn} < \text{Ni}$  (B)  $\text{Zn} < \text{Mg} < \text{Ni} < \text{Ca}$   
 (C)  $\text{Ni} < \text{Zn} < \text{Mg} < \text{Ca}$  (D)  $\text{Ca} < \text{Zn} < \text{Mg} < \text{Ni}$
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  $[\text{Ag}(\text{OH})_2]^-$
34. The element that usually does NOT show variable oxidation states is : [JEE-Main 2019]  
 (A) Cu (B) Sc (C) V (D) Ti
35. The correct order of the first ionization enthalpies is: [JEE-Main 2019]  
 (A)  $\text{Ti} < \text{Mn} < \text{Zn} < \text{Ni}$  (B)  $\text{Ti} < \text{Mn} < \text{Ni} < \text{Zn}$   
 (C)  $\text{Mn} < \text{Ti} < \text{Zn} < \text{Ni}$  (D)  $\text{Zn} < \text{Ni} < \text{Mn} < \text{Ti}$
36. Thermal decomposition of a Mn compound (X) at 513K results in compound Y,  $\text{MnO}_2$  and a gaseous product.  $\text{MnO}_2$  reacts with  $\text{NaCl}$  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  $\text{Cl}_2$

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

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

39. The third ionization enthalpy is minimum for: [Main Jan. 08, 2020]

- (A) Co (B) Fe (C) Ni (D) Mn

40. The atomic radius of Ag is closest to: [Main Jan. 07, 2020]

- (A) Au (B) Ni (C) Cu (D) Hg

41. Identify the element for which electronic configuration in +3 oxidation state is  $[Ar]3d^5$  :

[Main Sep. 1, 2021]

- (A) Ru (B) Mn (C) Co (D) Fe

42. Potassium permanganate on heating at 513 K gives a product which is:

[Main Aug. 27, 2021]

- (A) paramagnetic and colourless (B) diamagnetic and green  
 (C) diamagnetic and colourless (D) paramagnetic and green

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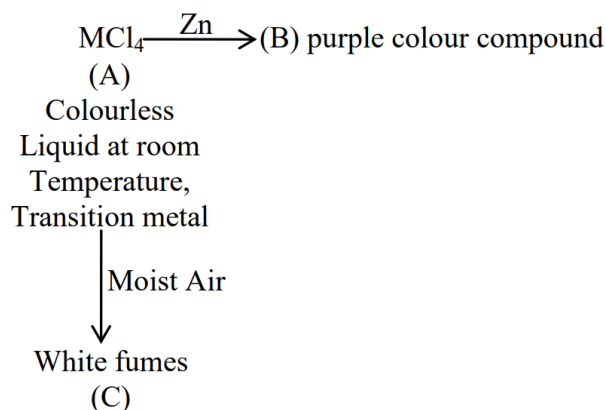
43. In the ground state of atomic Fe ( $Z = 26$ ), the spin-only magnetic moment is \_\_\_\_\_  $\times 10^{-1}$  BM. (Round off to the nearest integer).  
[Given :  $\sqrt{3} = 1.73, \sqrt{2} = 1.41$ ] [Main March 17, 2021 (III)]
44. The reaction of zinc with excess of aqueous alkali, evolves hydrogen gas and gives [Main July 29, 2022]  
(A)  $\text{Zn(OH)}_2$  (B)  $\text{ZnO}$  (C)  $[\text{Zn(OH)}_4]^{2-}$  (D)  $[\text{ZnO}_2]^{2-}$
45. The total number of Mn = O bonds in  $\text{Mn}_2\text{O}_7$  is [Main July 27, 2022]  
(A) 4 (B) 5 (C) 6 (D) 3
46. Dihydrogen reacts with  $\text{CuO}$  to give [Main June 28, 2022]  
(A)  $\text{CuH}_2$  (B)  $\text{Cu}$  (C)  $\text{Cu}_2\text{O}$  (D)  $\text{Cu(OH)}_2$
47. Among the following, which is the strongest oxidizing agent? [Main June 25, 2022]  
(A)  $\text{Mn}^{3+}$  (B)  $\text{Fe}^{3+}$  (C)  $\text{Ti}^{3+}$  (D)  $\text{Cr}^{3+}$
48. The disproportionation of  $\text{MnO}_4^{2-}$  in acidic medium resulted in the formation of two manganese compounds A and B. If the oxidation state of Mn in B is smaller than that of A, then the spin-only magnetic moment ( $\mu$ ) value of B in BM is \_\_\_\_\_. (Nearest integer)  
[Main July 28, 2022 (I)]
49. The spin-only magnetic moment value of the compound with strongest oxidizing ability among  $\text{MnF}_4$ ,  $\text{MnF}_3$  and  $\text{MnF}_2$  is \_\_\_\_\_ B.M. [nearest integer] [Main July 26, 2022 (II)]
50. The spin-only magnetic moment value of  $\text{M}^{3+}$  ion (in gaseous state) from the pairs  $\text{Cr}^{3+}/\text{Cr}^{2+}$ ,  $\text{Mn}^{3+}/\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{Co}^{3+}/\text{Co}^{2+}$  that has negative standard electrode potential is \_\_\_\_\_ B.M. [Nearest integer] [Main July 25, 2022 (II)]
51. The number of statement(s) correct from the following for copper (at no. 29) is/are \_\_\_\_\_. [Main June 27, 2022 (I)]  
(A) Cu (II) complexes are always paramagnetic  
(B) Cu (I) complexes are generally colourless  
(C) Cu(I) is easily oxidized  
(D) In Fehling solution, the active reagent has Cu (I)
52. Acidified potassium permanganate solution oxidises oxalic acid. The spin-only magnetic moment of the manganese product formed from the above reaction is \_\_\_\_\_. B.M. (Nearest Integer) [Main June 27, 2022 (I)]

EXERCISE-III  
JEE-ADVANCED

- Amongst the following identify the species with an atom in +6 oxidation state. [JEE 2000, 3/35]  
 (A)  $\text{MnO}_4^-$  (B)  $\text{Cr}(\text{CN})_6^{3-}$  (C)  $\text{NiF}_6^{2-}$  (D)  $\text{CrO}_2\text{Cl}_2$
- Write the balanced chemical equations for developing photographic films.
- In the standardization of  $\text{Na}_2\text{S}_2\text{O}_3$  using  $\text{K}_2\text{Cr}_2\text{O}_7$  by iodometry, the equivalent weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  is : [JEE 2001, 3/35]  
 (A) (molecular weight)/2, (molar mass)/2  
 (B) (molecular weight)/6  
 (C) (molecular weight)/3  
 (D) same as molecular weight
- Anhydrous ferric chloride is prepared by : [JEE 2002, 3/150]  
 (A) heating hydrated ferric chloride at a high temperature in a stream of air.  
 (B) heating metallic iron in a stream of dry chlorine.  
 (C) reaction of metallic iron with hydrochloric acid.  
 (D) reaction of metallic iron with nitric acid.
- When  $\text{MnO}_2$  is fused with  $\text{KOH}$ , a coloured compound is formed. The product and its colour is: [JEE 2003, 3/144]  
 (A)  $\text{K}_2\text{MnO}_4$ , green (B)  $\text{Mn}_2\text{O}_3$ , brown  
 (C)  $\text{Mn}_2\text{O}_4$ , black (D)  $\text{KMnO}_4$ , purple
- The product of oxidation of  $\text{I}^-$  with  $\text{MnO}_4^-$  in alkaline medium is : [JEE 2004, 3/144]  
 (A)  $\text{IO}_3^-$  (B)  $\text{I}_2$  (C)  $\text{IO}^-$  (D)  $\text{IO}_4^-$
- The pair of compounds having metals in their highest oxidation state is: [JEE 2004, 3/144]  
 (A)  $\text{MnO}_2$ ,  $\text{FeCl}_3$  (B)  $[\text{MnO}_4]^-$ ,  $\text{CrO}_2\text{Cl}_2$   
 (C)  $[\text{Fe}(\text{CN})_6]^{2-}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$  (D)  $[\text{NiCl}_4]^{2-}$ ,  $[\text{Ni}(\text{CO})_4]$ .
- Which of the following pair of compounds is expected to exhibit same colour in aqueous solution? [JEE 2005, 3/84]  
 (A)  $\text{FeCl}_3$ ,  $\text{CuCl}_2$  (B)  $\text{VOCl}_2$ ,  $\text{CuCl}_2$  (C)  $\text{VOCl}_2$ ,  $\text{FeCl}_2$  (D)  $\text{FeCl}_2$ ,  $\text{MnCl}_2$
- Give equations and describe the process for the developing of black and white photographic film. When sodium thiosulphate solution is treated with acidic solution turns milky white. Give the half reaction of the above described process. [JEE 2005, 4/60]

10.

[JEE 2005, 4/60]

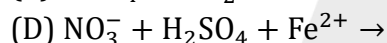
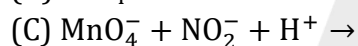
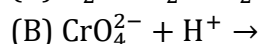
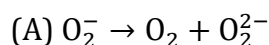


Identify (A), (B) and (C). Also explain colour difference between  $\text{MCl}_4$  and (B).

11. Match the reactions in Column I with nature of the reactions/type of the products in Column II.

[JEE 2007, 6/162]

Column I



Column II

(P) Redox reaction

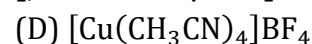
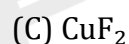
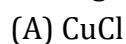
(Q) One of the products has trigonal planar structure

(R) Dimeric bridged tetrahedral metal ion

(S) Disproportionation

12. Among the following, the coloured compound is :

[JEE 2008, 3/163]



13. The oxidation number of Mn in the product of alkaline oxidative fusion of  $\text{MnO}_2$  is.

[JEE 2009, 4/160]

14. Reduction of the metal centre in aqueous permanganate ion involves: [JEE 2011, 4/180]

(A) 3 electrons in neutral medium

(B) 5 electrons in neutral medium

(C) 3 electrons in alkaline medium

(D) 5 electrons in acidic medium

15. The colour of light absorbed by an aqueous solution of  $\text{CuSO}_4$  is:

[JEE 2012, 3/136]

(A) orange-red

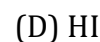
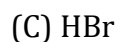
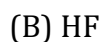
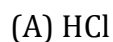
(B) blue-green

(C) yellow

(D) violet

16. Which of the following halides react(s) with  $\text{AgNO}_3$  (aq) to give a precipitate that dissolves in  $\text{Na}_2\text{S}_2\text{O}_3$  (aq) ?

[JEE 2012, 4/136]



17. Consider the following list of reagents:

[JEE(Advanced) 2014, 3/120]

Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ , alkaline  $\text{KMnO}_4$ ,  $\text{CuSO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{O}_3$ ,  $\text{FeCl}_3$ ,  $\text{HNO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$ . The total number of reagents that can oxidise aqueous iodide to iodine is

18. The correct statement(s) about  $\text{Cr}^{2+}$  and  $\text{Mn}^{3+}$  is (are) : [JEE(Advanced) 2015, 4/168]  
[Atomic numbers of Cr = 24 and Mn = 25 ]  
(A)  $\text{Cr}^{2+}$  is a reducing agent  
(B)  $\text{Mn}^{3+}$  is an oxidizing agent  
(C) Both  $\text{Cr}^{2+}$  and  $\text{Mn}^{3+}$  exhibit  $d^4$  electronic configuration  
(D) When  $\text{Cr}^{2+}$  is used as a reducing agent, the chromium ion attains  $d^5$  electronic configuration.
19.  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$  by using [JEE(Advanced) 2015, 4/168]  
(A)  $\text{H}_2\text{O}_2$  in presence of NaOH  
(B)  $\text{Na}_2\text{O}_2$  in water  
(C)  $\text{H}_2\text{O}_2$  in presence of  $\text{H}_2\text{SO}_4$   
(D)  $\text{Na}_2\text{O}_2$  in presence of  $\text{H}_2\text{SO}_4$
20. Fusion of  $\text{MnO}_2$  with KOH in presence of  $\text{O}_2$  produces a salt W. Alkaline solution of W upon electrolytic oxidation yields another salt X. The manganese containing ion's present in W and X, respectively, are Y and Z. Correct statement(s) is(are) [JEE(Advanced) 2019]  
(1) Y is diamagnetic in nature while Z is paramagnetic  
(2) In aqueous acidic solution, Y undergoes disproportionation reaction to give Z and  $\text{MnO}_2$   
(3) Both Y and Z are coloured and have tetrahedral shape  
(4) In both Y and Z,  $\pi$ -bonding occurs between p-orbitals of oxygen and d-orbitals of manganese
21. An acidified solution of potassium chromate was layered with an equal volume of amyl alcohol. When it was shaken after the addition of 1 mL of 3%  $\text{H}_2\text{O}_2$ , a blue alcohol layer was obtained. The blue color is due to the formation of a chromium (VI) compound 'X'. What is the number of oxygen atoms bonded to chromium through only single bonds in a molecule of X ?

[JEE(Advanced) 2020]

## NCERT EXAMPLER

## Multiple Choice Questions (Type-I)

- Electronic configuration of a transition element X in +3 oxidation state is  $[\text{Ar}]3d^5$ . What is its atomic number?  
(A) 25 (B) 26 (C) 27 (D) 24
- The electronic configuration of Cu(II) is  $3d^9$  whereas that of Cu(I) is  $3d^{10}$ . Which of the following is correct?  
(A) Cu (II) is more stable  
(B) Cu(II) is less stable  
(C) Cu(I) and Cu (II) are equally stable  
(D) Stability of Cu(I) and Cu(II) depends on nature of copper salts
- Metallic radii of some transition elements are given below. Which of these elements will have highest density?  

Element	Fe	Co	Ni	Cu
Metallic radii/pm	126	125	125	128

  
(A) Fe (B) Ni (C) Co (D) Cu
- Generally transition elements form coloured salts due to the presence of unpaired electrons. Which of the following compounds will be coloured in solid state?  
(A)  $\text{Ag}_2\text{SO}_4$  (B)  $\text{CuF}_2$  (C)  $\text{ZnF}_2$  (D)  $\text{Cu}_2\text{Cl}_2$
- On addition of small amount of  $\text{KMnO}_4$  to concentrated  $\text{H}_2\text{SO}_4$ , a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following.  
(A)  $\text{Mn}_2\text{O}_7$  (B)  $\text{MnO}_2$  (C)  $\text{MnSO}_4$  (D)  $\text{Mn}_2\text{O}_3$
- The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment.  
(A)  $3d^7$  (B)  $3d^5$  (C)  $3d^8$  (D)  $3d^2$
- Which of the following reactions are disproportionation reactions?  

(a) $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$	(b) $3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$
(c) $2\text{KMnO}_4 \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$	(d) $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+$

  
(A) a, b (B) a, b, c (C) b, c, d (D) a, d
- When  $\text{KMnO}_4$  solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because  
(A)  $\text{CO}_2$  is formed as the product. (B) Reaction is exothermic.  
(C)  $\text{MnO}_4^-$  catalyses the reaction. (D)  $\text{Mn}^{2+}$  acts as autocatalyst.

## (Organic Chemistry)

## d-BLOCK ELEMENTS

9.  $\text{KMnO}_4$  acts as an oxidising agent in acidic medium. The number of moles of  $\text{KMnO}_4$  that will be needed to react with one mole of sulphide ions in acidic solution is  
 (A)  $\frac{2}{5}$  (B)  $\frac{3}{5}$  (C)  $\frac{4}{5}$  (D)  $\frac{1}{5}$
10. Which of the following is amphoteric oxide?  
 $\text{Mn}_2\text{O}_7, \text{CrO}_3, \text{Cr}_2\text{O}_3, \text{CrO}, \text{V}_2\text{O}_5, \text{V}_2\text{O}_4$   
 (A)  $\text{V}_2\text{O}_5, \text{Cr}_2\text{O}_3$  (B)  $\text{Mn}_2\text{O}_7, \text{CrO}_3$  (C)  $\text{CrO}, \text{V}_2\text{O}_5$  (D)  $\text{V}_2\text{O}_5, \text{V}_2\text{O}_4$
11. Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. Which of the following is not the characteristic property of interstitial compounds?  
 (A) They have high melting points in comparison to pure metals.  
 (B) They are very hard.  
 (C) They retain metallic conductivity.  
 (D) They are chemically very reactive.
12. The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of  $\text{Cr}^{3+}$  ion is \_\_\_\_\_.  
 (A) 2.87 B.M. (B) 3.87 B.M. (C) 3.47 B.M. (D) 3.57 B.M.
13.  $\text{KMnO}_4$  acts as an oxidising agent in alkaline medium. When alkaline  $\text{KMnO}_4$  is treated with KI, iodide ion is oxidised to \_\_\_\_\_.  
 (A)  $\text{I}_2$  (B)  $\text{IO}^-$  (C)  $\text{IO}_3^-$  (D)  $\text{IO}_4^-$
14. Which of the following statements is not correct?  
 (A) Copper liberates hydrogen from acids.  
 (B) In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine.  
 (C)  $\text{Mn}^{3+}$  and  $\text{Co}^{3+}$  are oxidising agents in aqueous solution.  
 (D)  $\text{Ti}^{2+}$  and  $\text{Cr}^{2+}$  are reducing agents in aqueous solution.
15. When acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is added to  $\text{Sn}^{2+}$  salts then  $\text{Sn}^{2+}$  changes to  
 (A) Sn (B)  $\text{Sn}^{3+}$  (C)  $\text{Sn}^{4+}$  (D)  $\text{Sn}^+$
16. Highest oxidation state of manganese in fluoride is +4( $\text{MnF}_4$ ) but highest oxidation state in oxides is +7( $\text{Mn}_2\text{O}_7$ ) because  
 (A) fluorine is more electronegative than oxygen.  
 (B) fluorine does not possess d-orbitals.  
 (C) fluorine stabilises lower oxidation state.  
 (D) in covalent compounds fluorine can form single bond only while oxygen forms double bond.

17. Why is HCl not used to make the medium acidic in oxidation reactions of  $\text{KMnO}_4$  in acidic medium?
- (A) Both HCl and  $\text{KMnO}_4$  act as oxidising agents.  
(B)  $\text{KMnO}_4$  oxidises HCl into  $\text{Cl}_2$  which is also an oxidising agent.  
(C)  $\text{KMnO}_4$  is a weaker oxidising agent than HCl.  
(D)  $\text{KMnO}_4$  acts as a reducing agent in the presence of HCl.

## II. Multiple Choice Questions (Type-II)

**Note:** In the following questions two or more options may be correct.

18. Transition elements show magnetic moment due to spin and orbital motion of electrons. Which of the following metallic ions have almost same spin only magnetic moment?
- (A)  $\text{Co}^{2+}$  (B)  $\text{Cr}^{2+}$  (C)  $\text{Mn}^{2+}$  (D)  $\text{Cr}^{3+}$
19. In the form of dichromate, Cr(VI) is a strong oxidising agent in acidic medium but Mo(VI) in  $\text{MoO}_3$  and W(VI) in  $\text{WO}_3$  are not because
- (A) Cr(VI) is more stable than Mo(VI) and W(VI).  
(B) Mo(VI) and W(VI) are more stable than Cr(VI).  
(C) Higher oxidation states of heavier members of group-6 of transition series are more stable.  
(D) Lower oxidation states of heavier members of group-6 of transition series are more stable.
20. Which of the following ions show higher spin only magnetic moment value?
- (A)  $\text{Ti}^{3+}$  (B)  $\text{Mn}^{2+}$  (C)  $\text{Fe}^{3+}$  (D)  $\text{Co}^{3+}$
21. Transition elements form binary compounds with halogens. Which of the following elements will form  $\text{MF}_3$  type compounds?
- (A) Cr (B) Co (C) Cu (D) Ni
22. Which of the following will not act as oxidising agents?
- (A)  $\text{CrO}_3$  (B)  $\text{MoO}_3$  (C)  $\text{WO}_3$  (D)  $\text{CrO}_4^{2-}$

## III. Short Answer Type

23. Why does copper not replace hydrogen from acids?
24. Why  $E^0$  values for Mn, Ni and Zn are more negative than expected?
25. Why first ionisation enthalpy of Cr is lower than that of Zn ?
26. Transition elements show high melting points. Why?
27. When  $\text{Cu}^{2+}$  ion is treated with KI, a white precipitate is formed. Explain the reaction with the help of chemical equation.

28. Out of  $\text{Cu}_2\text{Cl}_2$  and  $\text{CuCl}_2$ , which is more stable and why?
29. When a brown compound of manganese (A) is treated with  $\text{HCl}$  it gives a gas (B). The gas taken in excess, reacts with  $\text{NH}_3$  to give an explosive compound (C). Identify compounds A, B and C.
30. Although fluorine is more electronegative than oxygen, but the ability of oxygen to stabilise higher oxidation states exceeds that of fluorine. Why?
31. Although  $\text{Cr}^{3+}$  and  $\text{Co}^{2+}$  ions have same number of unpaired electrons but the magnetic moment of  $\text{Cr}^{3+}$  is 3.87 B.M. and that of  $\text{Co}^{2+}$  is 4.87 B.M. Why?
32. Explain why does colour of  $\text{KMnO}_4$  disappear when oxalic acid is added to its solution in acidic medium.
33. When orange solution containing  $\text{Cr}_2\text{O}_7^{2-}$  ion is treated with an alkali, a yellow solution is formed and when  $\text{H}^+$  ions are added to yellow solution, an orange solution is obtained. Explain why does this happen?
34. A solution of  $\text{KMnO}_4$  on reduction yields either a colourless solution or a brown precipitate or a green solution depending on pH of the solution. What different stages of the reduction do these represent and how are they carried out?
35.  $E^0$  of Cu is +0.34 V while that of Zn is -0.76 V. Explain.
36. The halides of transition elements become more covalent with increasing oxidation state of the metal. Why?
37. While filling up of electrons in the atomic orbitals, the 4 s orbital is filled before the 3 d orbital but reverse happens during the ionisation of the atom. Explain why?
38. Reactivity of transition elements decreases almost regularly from Sc to Cu. Explain.

#### IV. Matching Type

**Note:** Match the items of Column I and Column II in the following questions.

39. Match the catalysts given in Column I with the processes given in Column II.

##### Column I (Catalyst)

- (A) Ni in the presence of hydrogen  
(B)  $\text{Cu}_2\text{Cl}_2$   
(C)  $\text{V}_2\text{O}_5$   
(D) Finely divided iron  
(E)  $\text{TiCl}_4 + \text{Al}(\text{CH}_3)_3$   
(F) Decomposition of  $\text{KClO}_3$

##### Column II (Process)

- (i) Ziegler Natta catalyst  
(ii) Contact process  
(iii) Vegetable oil to ghee  
(iv) Sandmeyer reaction  
(v) Haber's Process

40. Match the properties given in Column I with the metals given in Column II.

**Column I (Property)****Column II (Metal)**

- |  |          |
|--|----------|
| (A) An element which can show +8 oxidation state             | (i) Mn   |
| (B) 3 d series element that can show upto +7 oxidation state | (ii) Cr  |
| (C) 3 d series element with highest melting point            | (iii) Os |
|  | (iv) Fe  |

41. Match the solutions given in Column I and the colours given in Column II.

**Column I (Aqueous solution of salt)****Column II (Colour)**

- |   |                 |
|---|-----------------|
| (A) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ | (i) Green       |
| (B) $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ | (ii) Light pink |
| (C) $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ | (iii) Blue      |
| (D) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ | (iv) Pale green |
| (E) $\text{Cu}_2\text{Cl}_2$                  | (v) Pink        |
|   | (vi) Colourless |

42. Match the properties given in Column I with the metals given in Column II.

**Column I (Property)****Column II (Metal)**

- |   |          |
|---|----------|
| (A) Element with highest second ionisation enthalpy | (i) Co   |
| (B) Element with highest third ionisation enthalpy  | (ii) Cr  |
| (C) M in $\text{M}(\text{CO})_6$ is                 | (iii) Cu |
| (D) Element with highest heat of atomization        | (iv) Zn  |
|   | (v) Ni   |

**V. Assertion and Reason Type**

**Note:** In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (A) Both assertion and reason are true, and reason is the correct explanation of the assertion.  
 (B) Both assertion and reason are true but reason is not the correct explanation of assertion.  
 (C) Assertion is not true but reason is true.  
 (D) Both assertion and reason are false.

43. Assertion:  $\text{Cu}^{2+}$  iodide is not known.

Reason:  $\text{Cu}^{2+}$  oxidises  $\text{I}^-$  to iodine.

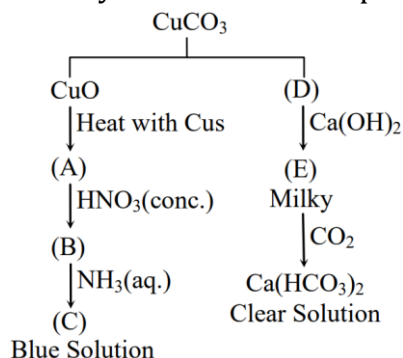
44. Assertion: Cu cannot liberate hydrogen from acids.

Reason: Because it has positive electrode potential.

45. Assertion: The highest oxidation state of osmium is +8.

Reason: Osmium is a 5d-block element.

46. Identify A to E and also explain the reactions involved.



47. When a chromite ore (A) is fused with sodium carbonate in free excess of air and the product is dissolved in water, a yellow solution of compound (B) is obtained. After treatment of this yellow solution with sulphuric acid, compound (C) can be crystallised from the solution. When compound (C) is treated with KCl, orange crystals of compound (D) crystallise out. Identify A to D and also explain the reactions.
48. When an oxide of manganese (A) is fused with KOH in the presence of an oxidising agent and dissolved in water, it gives a dark green solution of compound (B). Compound (B) disproportionates in neutral or acidic solution to give purple compound (C). An alkaline solution of compound (C) oxidises potassium iodide solution to a compound (D) and compound (A) is also formed. Identify compounds A to D and also explain the reactions involved.
49. (I) Answer the following questions :  
 (A) Which element of the first transition series has highest second ionisation enthalpy?  
 (B) Which element of the first transition series has highest third ionisation enthalpy?  
 (C) Which element of the first transition series has lowest enthalpy of atomisation?  
 (II) Identify the metal and justify your answer.  
 (A) Carbonyl  $\text{M}(\text{CO})_5$   
 (B)  $\text{MO}_3 \text{ F}$
50. Mention the type of compounds formed when small atoms like H, C and N get trapped inside the crystal lattice of transition metals. Also give physical and chemical characteristics of these compounds.
51. (a) Transition metals can act as catalysts because these can change their oxidation state. How does  $\text{Fe(III)}$  catalyse the reaction between iodide and persulphate ions?  
 (b) Mention any three processes where transition metals act as catalysts.
52. A violet compound of manganese (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of potassium nitrate to give compound (B). On heating compound (C) with conc.  $\text{H}_2\text{SO}_4$  and NaCl, chlorine gas is liberated and a compound (D) of manganese along with other products is formed. Identify compounds A to D and also explain the reactions involved.

## ANSWER KEY

## Do yourself - 1

<b>Question</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
<b>Answer</b>	B,C,D	A,B	A	A,B	B

## Do yourself - 2

<b>Question</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
<b>Answer</b>	A	A	B	D	A,B

## EXERCISE-I



<b>Q.1</b>	B	<b>Q.2</b>	A	<b>Q.3</b>	B	<b>Q.4</b>	A,B,C	<b>Q.5</b>	A,B	<b>Q.6</b>	B	<b>Q.7</b>	A,B,C,D
<b>Q.8</b>	A	<b>Q.9</b>	B	<b>Q.10</b>	A	<b>Q.11</b>	A,B, D	<b>Q.12</b>	A,B,C	<b>Q.13</b>	B,C	<b>Q.14</b>	B
<b>Q.15</b>	B	<b>Q.16</b>	A	<b>Q.17</b>	B	<b>Q.18</b>	D	<b>Q.19</b>	B	<b>Q.20</b>	C	<b>Q.21</b>	A,B,C
<b>Q.22</b>	A,B,C	<b>Q.23</b>	A	<b>Q.24</b>	A,B,C	<b>Q.25</b>	B	<b>Q.26</b>	A	<b>Q.27</b>	A	<b>Q.28</b>	B,C
<b>Q.29</b>	D	<b>Q.30</b>	A	<b>Q.31</b>	B	<b>Q.32</b>	A,C	<b>Q.33</b>	D	<b>Q.34</b>	A	<b>Q.35</b>	A,B
<b>Q.36</b>	C	<b>Q.37</b>	D	<b>Q.38</b>	A,B,C,D								
<b>Q.39</b>	C	<b>Q.40</b>	B	<b>Q.41</b>	C	<b>Q.42</b>	A	<b>Q.43</b>	A,B	<b>Q.44</b>	C	<b>Q.45</b>	D
<b>Q.46</b>	A	<b>Q.47</b>	A	<b>Q.48</b>	A,B,C	<b>Q.49</b>	A	<b>Q.50</b>	A,B	<b>Q.51</b>	B	<b>Q.52</b>	B,C
<b>Q.53</b>	C	<b>Q.54</b>	B	<b>Q.55</b>	A	<b>Q.56</b>	B	<b>Q.57</b>	D	<b>Q.58</b>	A	<b>Q.59</b>	B
<b>Q.60</b>	B	<b>Q.61</b>	A	<b>Q.62</b>	B	<b>Q.63</b>	C	<b>Q.64</b>	C	<b>Q.65</b>	B	<b>Q.66</b>	A
<b>Q.67</b>	A	<b>Q.68</b>	C										

## EXERCISE-II (JEE-Main)

<b>1.</b>	(A)	<b>2.</b>	(A)	<b>3.</b>	(A)	<b>4.</b>	(A)	<b>5.</b>	(C)	<b>6.</b>	(A)	<b>7.</b>	(A)
<b>8.</b>	(D)	<b>9.</b>	(B)	<b>10.</b>	(D)	<b>11.</b>	(C)	<b>12.</b>	(C)	<b>13.</b>	(D)	<b>14.</b>	(A)
<b>15.</b>	(D)	<b>16.</b>	(B)	<b>17.</b>	(B)	<b>18.</b>	(A)	<b>19.</b>	(A)	<b>20.</b>	(B)	<b>21.</b>	(A)
<b>22.</b>	(D)	<b>23.</b>	(D)	<b>24.</b>	(D)	<b>25.</b>	(A)	<b>26.</b>	(D)	<b>27.</b>	(D)	<b>28.</b>	(B)
<b>29.</b>	(C)	<b>30.</b>	(D)	<b>31.</b>	(A)	<b>32.</b>	(C)	<b>33.</b>	(A)	<b>34.</b>	(B)	<b>35.</b>	(B)
<b>36.</b>	(A)	<b>37.</b>	(C)	<b>38.</b>	(C)	<b>39.</b>	(B)	<b>40.</b>	(A)	<b>41.</b>	(D)	<b>42.</b>	(D)
<b>43.</b>	(49)	<b>44.</b>	(C)	<b>45.</b>	(C)	<b>46.</b>	(B)	<b>47.</b>	(A)	<b>48.</b>	(4)	<b>49.</b>	(5)
<b>50.</b>	(4)	<b>51.</b>	(3)	<b>52.</b>	(6)								

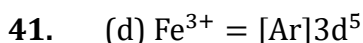
- $$\therefore \text{Ti} < \text{Mn} < \text{Ni} < \text{Zn}$$

- $$\text{MnO}_2 + 4\text{NaCl} + 4\text{H}_2\text{SO}_4 \rightarrow \text{MnCl}_2 + 4\text{NaHSO}_4 + \text{Cl}_2 + 2\text{H}_2\text{O}$$
- Conc. (Z)
- Pungent gas

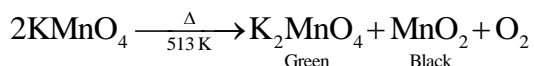
- |     |     |  |  |
|-----|-----|--|--|
| 38. | (C) | <p><b>Manganate</b></p> $\text{MnO}_4^{2-}$  <p>Paramagnetic,<br/>green in colour,<br/>Tetrahedral &amp;<br/>contains<br/><math>P\pi - d\pi</math> bond</p> | <p><b>Permanganate</b></p> $\text{MnO}_4^-$  <p>Diamagnetic,<br/>purple in colour,<br/>Tetrahedral &amp;<br/>contains<br/><math>P\pi - d\pi</math> bond</p> |
|-----|-----|--|--|

Manganate ion is paramagnetic while permanganate ion is diamagnetic.

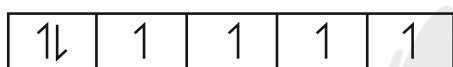
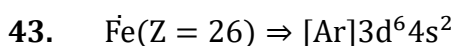
- 40.** (a) Atomic size of elements of 4d and 5d transition series are nearly same due to lanthanide contraction.



42. (d) Potassium permanganate on heating at 513 K gives potassium manganate (
- $\text{K}_2\text{MnO}_4$
- ) and its colour is green.

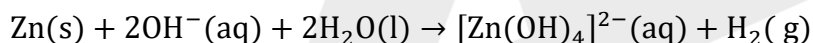


In  $\text{K}_2\text{MnO}_4$ , manganese oxidation state is +6 and hence, it has one unpaired electron and is paramagnetic.



Number of unpaired electrons = 4

44. (c) Zinc dissolves in excess of aqueous alkali.

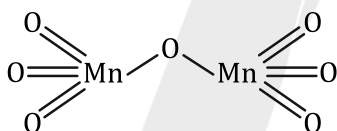


Tetrahydroxozincate (II) ion

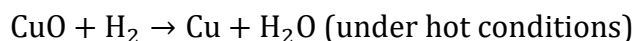
$\text{ZnO}_2^{2-}$  is anhydrous form of  $[\text{Zn(OH)}_4]^{2-}$

So in aqueous medium best answer of this question is  $[\text{Zn(OH)}_4]^{2-}$ .

45. (c) In manganese heptoxide, there are 6, Mn = O bonds.

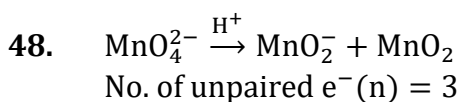


46. (b) Copper gets reduced and hydrogen gets oxidised

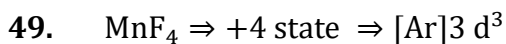


47. (a) Strongest oxidising agent has highest reduction potential value.

$$E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}} = 1.51 \text{ V (highest)}$$



$$\therefore \mu = \sqrt{n(n+2)} = \sqrt{15} = 3.877 \text{ B.M.}$$



(Strongest O.A)



For  $n = 4$ ,

$$\therefore \mu_5 = \sqrt{4(4+2)} = \sqrt{24} = 4.89 = 5$$

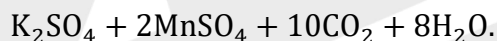
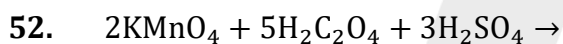
50. In case of conversion of  $\text{Cr}^{3+} \rightarrow \text{Cr}^{2+}$  the  $e^-$  is added to  $e_g$  orbital, hence electrode potential is negative.

$$E_{\text{Cr}^{+3}/\text{Cr}^{+2}}^\circ = -0.41 \text{ V}$$

$$[\text{Cr}^{+3}] = 4s^0 3d^3$$

$$\mu = \sqrt{n(n+2)} \text{ B.M} = \sqrt{15} \text{ B.M} \approx 4 \text{ B.M}$$

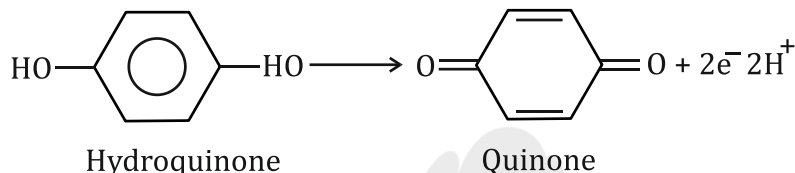
51. A, B, C are correct and D is incorrect because Fehling solution has Cu (II).



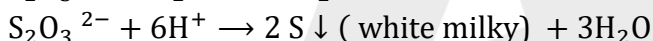
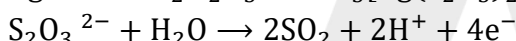
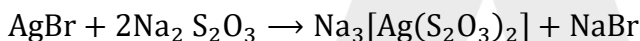
$\text{Mn}^{2+}$  has 5 unpaired electrons, therefore, the magnetic moment  $= \sqrt{5(5+2)} = \sqrt{35} \text{ BM}$ .

## EXERCISE-III (JEE-ADVANCED)

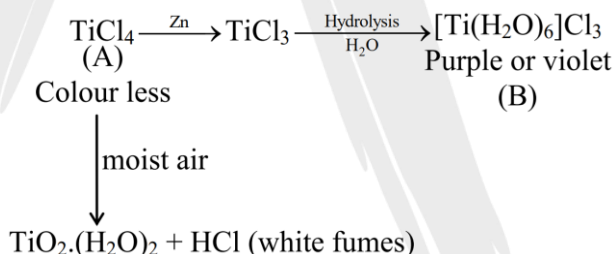
1. (D)  
 2.  $C_6H_4(OH)_2 + 2AgBr \rightarrow 2Ag + C_6H_4O_2 + 2HBr$   
 $AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$   
 3. (B) 4. (B) 5. (A) 6. (A) 7. (B) 8. (B)  
 9. Developer is usually a weak reducing agent like potassium ferrous oxalate, an alkaline solution of pyrogallol or an alkaline solution of quinol.  
 In the process of development of the photographic film, the exposed/activated AgBr grains are preferentially reduced by one of the reducing agent described above.



The photographic film is then fixed by washing with hypo solution to remove the unreduced AgBr grains from the film.

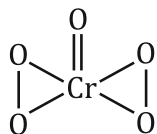


10. (A) is  $TiCl_4$  as it has no unpaired electron and is liquid at room temperature on account of covalent character because of high polarising power of  $Ti^{+4}$  being covalent gets hydrolysed forming  $TiO_2 \cdot (H_2O)_2$  and  $HCl(B)$  which fumes in air.  
 In  $[Ti(H_2O)_6]Cl_3$  complex  $Ti(III)$  has one unpaired electron ( $3d^1$ ) which gives violet/purple colour to d-d transition.



11. (A) – P, S; (B) – R; (C) – P, Q; (D) – (P).  
 12. (C) 13. 6 14. (A, C, D)/(A, D) 15. (A) 16. (A, C, D)  
 17. 7 18. (A, B, C) 19. (C, D) 20. (2,3,4)  
 21. 4

Blue colour compound of 'Cr' is  $CrO_5$ .



Oxygen atoms bonded to chromium through only single bonds = 4

## NCERT EXAMPLER

## I. Multiple Choice Questions (Type-I)

1. (B) 2. (A) 3. (D) 4. (B) 5. (A) 6. (B) 7. (A)  
 8. (D) 9. (A) 10. (A) 11. (D) 12. (B) 13. (C) 14. (A)  
 15. (C) 16. (D) 17. (B)

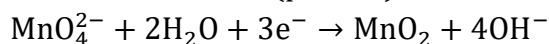
## II. Multiple Choice Questions (Type-II)

18. (A),(D) 19. (B), (C) 20. (B), (C) 21. (A), (B)  
 22. (B), (C)

## III. Short Answer Type

23. Cu shows positive  $E^\ominus$  value.
24. Hint : Negative  $E^\ominus$  values for  $Mn^{2+}$  and  $Zn^{2+}$  are related to stabilities of half filled and fully filled configuration respectively. But for  $Ni^{2+}$ ,  $E^\ominus$  value is related to the highest negative enthalpy of hydration.
25. Ionisation enthalpy of Cr is lower due to stability of d5 and the value for Zn is higher because its electron comes out from 4 s orbital.
26. The high melting points of transition metals are attributed to the involvement of greater number of electrons in the interatomic metallic bonding from (n-1) d-orbitals in addition to ns electrons
27. Hint :  $Cu^{2+}$  gets reduced to  $Cu^+$   
 $2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$   
 (white precipitate)
28. Hint :  $CuCl_2$  is more stable than  $Cu_2Cl_2$ . The stability of  $Cu^{2+}$  (aq.) rather than  $Cu^+$  (aq.) is due to the much more negative  $\Delta H^\ominus$  of  $Cu^{2+}$  (aq.) than  $Cu^+$  (aq.).
29. A =  $MnO_2$  B =  $Cl_2$  C =  $NCl_3$   
 $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$   
 (A) (B)  
 $NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$   
 (excess) (C)
30. Hint: It is due to the ability of oxygen to form multiple bonds to metals.
31. Hint: Due to symmetrical electronic configuration there is no orbital contribution in  $Cr^{3+}$  ion. However appreciable orbital contribution takes place in  $Co^{2+}$  ion.
32.  $KMnO_4$  acts as oxidising agent. It oxidises oxalic acid to  $CO_2$  and itself changes to  $Mn^{2+}$  ion which is colourless.  
 $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$   
 (Coloured) (Colourless)
33.  $Cr_2O_7^{2-}$   
 Dichromate Chromate  
 (Orange) (Yellow)
34. Oxidising behaviour of  $KMnO_4$  depends on pH of the solution. In acidic medium ( $pH < 7$ )  
 $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$   
 (Colourless)  
 In alkaline medium ( $pH > 7$ )  
 $MnO_4^- + e^- \rightarrow MnO_4^{2-}$

(Green)

In neutral medium ( $\text{pH} = 7$ )

(Brown precipitate)

35. Hint: High ionisation enthalpy to transform  $\text{Cu(s)}$  to  $\text{Cu}^{2+}(\text{aq})$  is not balanced by its hydration enthalpy. However, in case of Zn after removal of electrons from 4 s-orbital, stable  $3\text{d}^{10}$  configuration is acquired.
36. As the oxidation state increases, size of the ion of transition element decreases. As per Fajan's rule, as the size of metal ion decreases, covalent character of the bond formed increases.
37.  $n + l$  rule : For  $3\text{d}$   $n + l = 5$   $4\text{s}$   $n + l = 4$   
So electron will enter in 4 s orbital.  
Ionisation enthalpy is responsible for the ionisation of atom. 4 s electrons are loosely held by the nucleus. So electrons are removed from 4 s orbital prior to 3 d.
38. Hint : It is due to regular increase in ionisation enthalpy.

**IV. Matching Type**

39. (A)  $\rightarrow$  (iii) ; (B)  $\rightarrow$  (iv) ; (C)  $\rightarrow$  (ii) ; (D)  $\rightarrow$  (v) ; (E)  $\rightarrow$  (i)
40. (A)  $\rightarrow$  (iii) ; (B)  $\rightarrow$  (i) ; (C)  $\rightarrow$  (ii)
41. (A)  $\rightarrow$  (iv) ; (B)  $\rightarrow$  (i) ; (C)  $\rightarrow$  (ii) ; (D)  $\rightarrow$  (v) ; (E)  $\rightarrow$  (vi)
42. (A)  $\rightarrow$  (iii) ; (B)  $\rightarrow$  (iv) ; (C)  $\rightarrow$  (ii) ; (D)  $\rightarrow$  (i)

**V. Assertion and Reason Type**

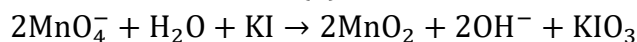
43. (A) 44. (A) 45. (B)

**VI. Long Answer Type**

46. A = Cu B =  $\text{Cu}(\text{NO}_3)_2$  C =  $[\text{Cu}(\text{NH}_3)_4]$  D =  $\text{CO}_2$   
E =  $\text{CaCO}_3$  F =  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$  G =  $\text{Ca}(\text{HCO}_3)_2$   
 $\text{CuCO}_3 \rightarrow \text{CuO} + \text{CO}_2$   
 $\text{CuO} + \text{CuS} \rightarrow \text{Cu} + \text{SO}_2$   
(A)  
 $\text{Cu} + 4\text{HNO}_3(\text{Conc}) \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 2\text{H}_2\text{O}$   
(B)  
 $\text{Cu}^{2+} + \text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]$   
(B) (C)  
 $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$   
(D) (E)  
 $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca}(\text{HCO}_3)_2$
47. A =  $\text{FeCr}_2\text{O}_4$  B =  $\text{Na}_2\text{CrO}_4$  C =  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  D =  $\text{K}_2\text{Cr}_2\text{O}_7$   
 $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$   
(A) (B)  
 $2\text{NaCrO}_4 + 2\text{H}^+ \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{Na}^+ + \text{H}_2\text{O}$   
 $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$   
(C) (D)
48. A =  $\text{MnO}_2$  (B)  $\text{K}_2\text{MnO}_4$  (C)  $\text{KMnO}_4$  (D)  $\text{KIO}_3$   
 $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \rightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$   
(A) (B)



(C)



(A)

(D)

49. (a) (A) Cu, because the electronic configuration of Cu is  $3d^{10}4s^1$ . So second electron needs to be removed from completely filled d-orbital.

(B) Zn [Hint : As above]

(C) Zn [Hint : No unpaired electron for metallic bonding]

(b) (A)  $\text{Fe}(\text{CO})_5$  [Hint : EAN rule](B)  $\text{MnO}_3\text{F}$  [Hint : Mn shows +7 oxidation state; d-electrons are not involved in bonding.]

50. Interstitial compounds.

Characteristic properties :

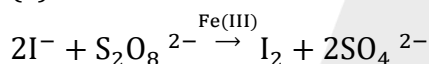
(A) High melting points, higher than those of pure metals.

(B) Very hard.

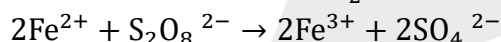
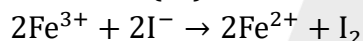
(C) Retain metallic conductivity.

(D) Chemically inert.

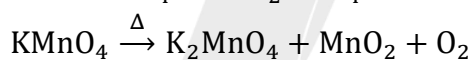
51. (a) Reaction between iodide and persulphate ions is :



Role of Fe (III) ions :

(b) (A) Vanadium (V) oxide in contact process for oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ .(B) Finely divided iron in Haber's process in conversion of  $\text{N}_2$  and  $\text{H}_2$  to  $\text{NH}_3$ .(C)  $\text{MnO}_2$  in preparation of oxygen from  $\text{KClO}_3$ .

52. A =  $\text{KMnO}_4$  B =  $\text{K}_2\text{MnO}_4$  C =  $\text{MnO}_2$  D =  $\text{MnCl}_2$



(A)

(B)

(C)



(D)