

## d-Block Elements

There are six sections, Section 1 discusses general properties of d-Block Elements, Section 2 discusses chromium, Section 3 discusses Manganese, Section 4 discusses Iron, Cobalt Nickel groups, Section 5 discusses Copper and Section 6 is on Zinc group.

### GENERAL PROPERTIES OF TRANSITION ELEMENTS

### Section - 1

Three series of elements are formed by filling the  $3d$ ,  $4d$  and  $5d$  shells of elements, together called the d-block elements (Group 3-12). They are often called '*transition elements*' because their position is between the s-block and p-block. Strictly speaking, a transition element is the one which has incompletely filled  $d$ -orbitals in its ground state or in any one of its oxidation states. Thus Zn, Cd, Hg of group 12 having full  $d^{10}$  configuration are not regarded as transition metals. Compounds of these elements are thus not typical and show some differences from the others. In general the electronic configuration of these elements is  $(n-1)d^{1-10}ns^{1-2}$ . In the case of Cr and Cu, the configuration is  $d^5s^1$  and  $d^{10}s^1$  instead of  $d^4s^2$  and  $d^9s^2$  respectively. This is because of the additional stability when the d-orbitals are exactly half filled or completely filled.

### Oxidation states and their stability

Transition elements show a great variety of oxidation state. The prominent oxidation states are shown in the following table:

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronic structure	$d^1s^2$	$d^2s^2$	$d^3s^2$	<del><math>d^4s^2</math></del> $d^5s^1$	$d^5s^2$	$d^6s^2$	$d^7s^2$	$d^8s^2$	<del><math>d^9s^2</math></del> $d^{10}s^1$	$d^{10}s^2$
Oxidation states	II III	II III IV	II III IV IV	I II III IV V VI	II III IV V VI VII	II III IV V VI	II III IV V	II III IV	I II III	II

The various oxidation states show a difference in stability. In general the second and third row elements exhibit higher coordination numbers and their higher oxidation states are more stable than the corresponding first row elements. This is interesting because in p-block elements the lower oxidation states are favoured by the heavier elements (due to inert pair effect).

### Atomic and Ionic Sizes

The covalent radii decreases from left to right across the period in d-block until near the end when the size increases slightly.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
1.62	1.45	1.34	1.29	-	1.24	1.25	1.28
La	Zr	Ta	W	Re	Os	Ir	Pt
1.69	1.45	1.34	1.30	-	1.26	1.26	1.29

14 Lanthanide elements

On going down the group the size increases as expected. But it is noticed that the increase in radius between the second and third member of a group is virtually negligible. This is due to the intervention of the  $4f$  orbitals which must be filled before the  $5d$  series begins. The  $f$ -shells shield the nuclear charge poorly as compared to  $s$ ,  $p$ ,  $d$  shells and thus lead to a decrease in radii called **Lanthanoid contraction** or  **$f$ -block contraction** which compensates for the expected increase in atomic size with increasing atomic number.

### Melting and boiling points

The transition metals (except Zn, Cd and Hg) are very much hard and have high m.p. and b.p.. They typically melt over  $1000^{\circ}\text{C}$ . Zn, Cd and Hg behave abnormally (Hg is in fact a liquid with m.p.  $-38^{\circ}\text{C}$ ) because they have a complete  $d$  shell and  $d$  electrons do not participate in metallic bonding.

### Density

Due to low atomic volumes as compared with Group 1 and 2 metals, they have high densities (almost all have greater than  $5\text{gcm}^{-3}$ ). To get a feel of high densities of Os ( $22.57\text{g/cc}$ ) and Ir ( $22.61\text{g/cc}$ ), a football of Os or of diameter 30cm would weight 320kg !

### Colour

Many ionic and covalent compounds of transition elements are coloured (In contrast those of  $s$  and  $p$  block are generally white). Colour arises when a compound is able to absorb some wavelength in the visible region of the spectrum. The colour of the compound is then that of the transmitted light i.e. the complementary colour to the colour of the light absorbed. Ions having  $d^{10}$  or  $d^0$  configuration are usually uncoloured. Thus  $\text{ZnSO}_4$  and  $\text{TiO}_2$  are colourless because in  $\text{Zn}^{2+}(d^{10})$  and  $\text{Ti}^{4+}(d^0)$  it is not possible to promote electrons within the  $d$ -level.

Another reason for colour can be charge transfer from one atom to another as occurs in  $\text{MnO}_4^-$  (intense purple).

### Magnetic Properties

When an external magnetic field  $H$  is applied on a substance, the intensity of field inside it may be greater than or less than  $H$ . If the field is greater than  $H$ , the substance is paramagnetic and if the field is less than  $H$  it is diamagnetic. Ferromagnetic materials are a special case of paramagnetism in which the moments on individual atoms become aligned and all point in the same direction increasing the magnetic susceptibility drastically. Fe, Co and Ni are ferromagnetic. Antiferromagnetism is just opposite to ferromagnetism when the moments on individual atoms are aligned in the opposite direction to that of  $H$ . It occurs in several simple salts of  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$  and  $\text{Gd}^{3+}$ . Since ferromagnetism and antiferromagnetism depend on orientation they disappear in solution.

Paramagnetism arises from the presence of unpaired electrons each having a magnetic moment due to its spin and due to its orbitals angular momentum. The 'spin only' formula is :

$\mu_s = \sqrt{n(n+2)}$ , where  $n$  is the number of unpaired electrons. The unit is Bohr Magneton (BM). For the 3- $d$  series effect of orbitals angular momentum is effectively negligible.

### Catalytic Properties

Transition elements and their compounds are important catalysts. In some cases they form variable valency unstable intermediates and in other cases they provide a suitable reaction surface. For example,  $\text{TiCl}_3$  is used as 'Ziegler-Natta catalyst' in the production of polythene,  $\text{MnO}_2$  is used as a catalyst to decompose  $\text{KClO}_3$  to give  $\text{O}_2$ , Pd is used for hydrogenation and  $\text{V}_2\text{O}_5$  converts  $\text{SO}_2$  to  $\text{SO}_3$  in the Contact Process for which Fe was formerly used.

### Complexes

The transition elements have an unparalleled tendency to form coordination compounds with lewis bases called *ligands*. Some example are  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ . The reason for this is that transition elements have small, highly charged ions and vacant low energy orbitals to accept lone pairs of electrons donated by other groups.

### IN-CHAPTER EXERCISE - A

1. Why do second and third rows of transition elements resemble each other more closely than the first row?
2. Give reasons :
  - (i) Most transition metals show paramagnetic behaviours.
  - (ii) Transition metal and their many compounds are coloured.

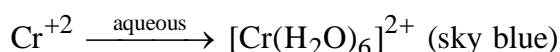
## CHROMIUM &amp; ITS COMPOUNDS

## Section - 2

Chromium metal is produced on a large scale from the ore chromite ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  or  $\text{FeCr}_2\text{O}_4$ ). It is unreactive or passive at low temperature due to the formation of a protective coating of oxide,  $\text{Cr}_2\text{O}_3$ . Thus it is used in electroplating to prevent corrosion of iron articles. For Cr the +II, +III, +VI states are well known. Cr(+II) is reducing, Cr(+III) is the most stable and important, and Cr(+VI) is strongly oxidising.

**Cr<sup>+II</sup> state (Chromous Compounds)**

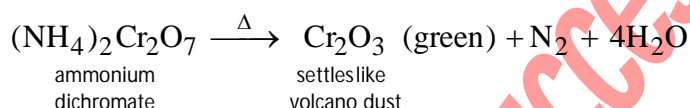
$\text{Cr}^{+2}$  is one of the strongest reducing agent known in aqueous solution. The  $\text{Cr}^{+2}$  ion is blue coloured in aqueous solution.



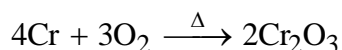
Important compounds are  $\text{CrCl}_2$  and  $\text{Cr}_2(\text{CH}_3\text{COO})_4$ .

**Cr<sup>+III</sup> state (Chromic Compounds)**

It is the most stable and important state of chromium. *Chromic Oxide* ( $\text{Cr}_2\text{O}_3$ ) is used as a green pigment in paint, rubber, cement and prepared in the well known volcano experiment :



The heat produced continues the above reaction on its own. Also,

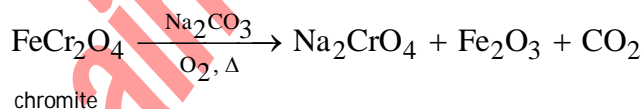


*Chromic chloride* ( $\text{CrCl}_3$ ) is a solid which forms red-violet flakes and dissolves in water to form violet coloured solutions.

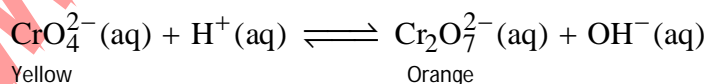
**Cr<sup>+VI</sup> State**

Few  $\text{Cr}^{+6}$  compounds are known. These are very strong oxidising agents and include chromates  $[\text{CrO}_4]^{2-}$ , dichromates  $[\text{Cr}_2\text{O}_7]^{2-}$  and chromium trioxide  $\text{CrO}_3$ .

*Sodium chromate* ( $\text{Na}_2\text{CrO}_4$ ) is a yellow solid prepared by fusing chromite with  $\text{Na}_2\text{CO}_3$ .

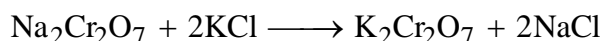


On acidifying sodium chromate, an orange coloured solid sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7$ ) is obtained while this sodium dichromate turns orange in basic solutions due to reformation of  $\text{CrO}_4^{2-}$ . The reversible reaction is thus represented by :

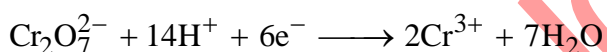


**Potassium dichromate [ $K_2Cr_2O_7$ ]**

To prepare potassium dichromate,  $Na_2Cr_2O_7$  is first prepared from chromite as discussed above and then it is converted to  $K_2Cr_2O_7$  by a KCl solution.



1. Action of heat :  $K_2Cr_2O_7 \xrightarrow{\Delta} K_2CrO_4 + \underset{\text{Green solid}}{Cr_2O_3} + O_2 \uparrow$
2. Potassium dichromate is widely used as an oxidizing agent and a primary standard. The orange coloured  $K_2Cr_2O_7$  solution gets decolourised and  $Cr^{2+}$  is formed.

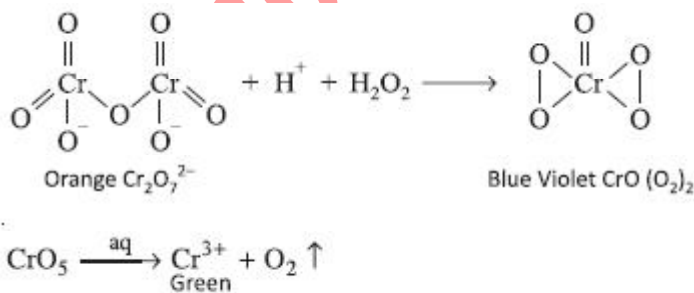


Thus it oxidises HCl to  $Cl_2$ , KI to  $I_2$ , and  $FeSO_4$  to  $Fe_2(SO_4)_3$ . Note that  $K_2Cr_2O_7$  is preferred to  $Na_2Cr_2O_7$  for use in volumetric analysis because the Na compound is hygroscopic whilst the K compound is not.

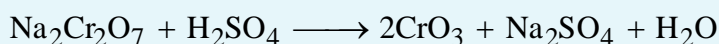
3. The **Chromyl Chloride Test** is used to detect  $Cr_2O_7^{2-}$  when treated with conc. HCl or any chloride in conc.  $H_2SO_4$ , reddish brown vapours of chromyl chloride are obtained.



4. When hydrogen peroxide is added to  $K_2Cr_2O_7/H^+$ , a deep blue - violet peroxo compound  $CrO_5$  is formed. This decomposes rapidly into  $Cr^{3+}$  and  $O_2$  in aqueous solution.



**Note :** *Chromic acid* ( $CrO_3$ ) is a bright orange solid used to clean laboratory glassware. It is obtained by adding conc.  $H_2SO_4$  to a saturated solution of sodium dichromate.



## MANGANESE &amp; IT'S COMPOUNDS

## Section - 3

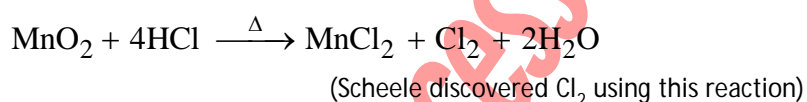
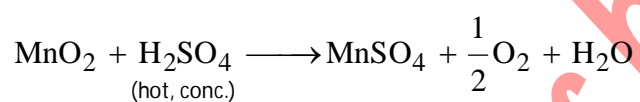
Manganese is mined as the ore pyrolusite ( $\text{MnO}_2$ ) and is obtained by electrolysis of aqueous solution of  $\text{MnSO}_4$ . 95% of it is used in the steel industry to produce alloys.

 **$\text{Mn}^{+II}$  State (Manganous)**

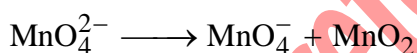
The (+II) state is the most stable and common state. Manganous salts like  $\text{MnCl}_2$ ,  $\text{MnSO}_4$  are soluble in water and form pink coloured solutions of  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  while  $\text{MnCO}_3$  is sparingly soluble.

 **$\text{Mn}^{+IV}$  State**

Very few  $\text{Mn}(+IV)$  compounds are known.  $\text{MnO}_2$  is the most important oxide in the group and is commercially important. It occurs naturally as black coloured pyrolusite ore.

 **$\text{Mn}^{+VI}$  State**

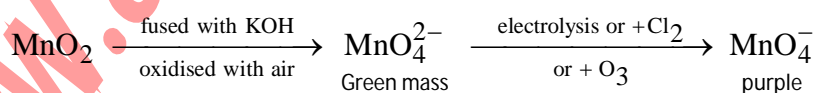
The only example in this category is dark green coloured manganate ion  $\text{MnO}_4^{2-}$ . It is a strong oxidising agent and only stable in very strong alkali solutions. In dilute alkali, water (neutral) or acidic solution it disproportionates.

 **$\text{Mn}^{+VII}$  State**

$\text{Mn}^{+7}$  state is obtained when all the electrons of  $d^5s^2$  in Mn are used for bonding. It is not common but very well known as the purple coloured permanganate ion ( $\text{MnO}_4^-$ ). The colour arises despite the  $d^0$  configuration due to charge transfer.

**Potassium Permanganate [ $\text{KMnO}_4$ ]**

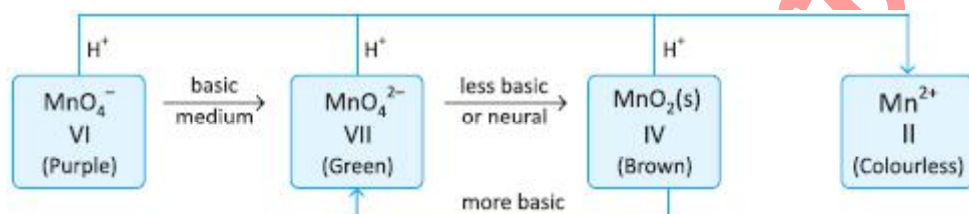
$\text{KMnO}_4$  exists as deep purple black prism with greenish lustre and is moderately soluble in water at room temperature. It is manufactured on a large scale as follows :



1.  $\text{KMnO}_4$  is stored in dark bottles as its decomposition to  $\text{MnO}_2$  is catalysed by sunlight.



2.  $\text{KMnO}_4$  is widely used as an oxidising agent in both preparative and qualitative chemistry. In acidic solution it is reduced to  $\text{Mn}^{2+}$ , to  $\text{MnO}_4^{2-}$  in alkaline solutions and to  $\text{MnO}_2$  in neutral or slightly basic solutions thus oxidising  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ,  $\text{I}^-$  to  $\text{I}_2$  and  $\text{H}_2\text{S}$  to  $\text{S}$ .
3. With larger amounts of  $\text{KMnO}_4$ , an explosive oil  $\text{Mn}_2\text{O}_7$  is formed. (Do not try this)
- The following diagram will help you to memorize the interconnection between various manganese compounds :



### IN-CHAPTER EXERCISE - B

- Complete and balance the following equations.
  - $\text{K}_2\text{Cr}_2\text{O}_7 + \dots + 4\text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O} + 3\text{I}_2$
  - $\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow[400^\circ\text{C}]{\Delta}$
  - $\text{KMnO}_4 \xrightarrow[200^\circ\text{C}]{\Delta}$
  - $\text{MnO}_4^- + \text{AsO}_3^- + \text{H}^+ \longrightarrow$
  - $\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{NH}_4\text{Cl}} \xrightarrow{\Delta} (\text{gas}) + (\text{green}) \xrightarrow[\Delta]{\text{Al}} (\text{metal}) + (\text{oxide})$
- Account for the following observations and write balanced chemical equations for them.
  - The yellow colour of solutions change to orange on acidification.
  - Acidified solution of ions form a deep blue colour with  $\text{H}_2\text{O}_2$ .
- When a white crystalline compound X is heated with  $\text{K}_2\text{Cr}_2\text{O}_7$  and concentrated  $\text{H}_2\text{SO}_4$ , a reddish brown gas A is evolved. On passing A into caustic soda solution, a yellow coloured solution of B is obtained. Neutralising the solution of B with acetic acid and on subsequent addition of lead acetate, a yellow precipitate C is obtained. When X is heated with  $\text{NaOH}$  solution, a colourless gas is evolved and on passing this gas into  $\text{K}_2\text{HgI}_4$  solution, a reddish brown precipitate D is formed. Identify A, B, C, D and X. Write the equations of reaction involved.

4. *Pyrolusite on heating with KOH in the presence of the air gives a dark brown compound A. When ozonized oxygen is passed through a solution of A, a purple coloured compound B is formed. Write balanced chemical equations for the formation of B.*
5. *Acidified  $K_2Cr_2O_7$  solution turns green when sodium sulphite is added to it. Explain.*

## IRON, COBALT & NICKEL GROUPS

## Section - 4

Group 8	Group 9	Group 10
Fe	Co	Ni
Ru	Rh	Pd
Os	Ir	Pt

These nine elements earlier made up Group VIII in the old Mendeleev periodic table. The horizontal similarities between these elements are greater than anywhere else in the periodic table. Fe, Co and Ni are together called 'Ferrous metals' and Ru, Rh, Pd, Os, Ir, Pt are known as 'platinum metals'.

### [A] Iron and Its Compounds

Fe is a silvery metal which is not very hard and quite reactive. It is used in large quantities in steel making. Its biological importance is as an electron carrier in plants and animals, as haemoglobin in mammals, as nitrogenase to fix bacteria and many more. Fe is strongly ferromagnetic but the ferromagnetism is lost above the Curie Temperature which is  $700^\circ\text{C}$  for Fe.

Iron is passivated by strong oxidising agents like conc.  $\text{HNO}_3$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  due to the formation of a protective coat of oxide ( $\text{Fe}_2\text{O}_3$ ) while with dilute acids Fe is oxidised to  $\text{Fe}^{2+}$ . Finely divided iron combines with the ligand CO forming  $[\text{Fe}(\text{CO})_5]$  which is liquid at room temperature.

Rusting of iron is a special case of corrosion and is of great importance. Rusting occurs in the presence of  $\text{O}_2$ ,  $\text{H}_2\text{O}$  and  $\text{H}^+$  due to the formation of an oxide film of  $\text{Fe}_2\text{O}_3$  which is not protective and the corrosion continues. To prevent corrosion,  $\text{O}_2$  and  $\text{H}_2\text{O}$  must be excluded. This is done by electroplating Fe with a thin layer of Sn (tin plating), dipping the Fe in molten zinc (hot dipping), electroplating with Zn (galvanising) or painting with red lead.

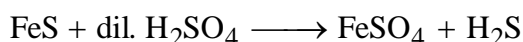
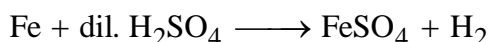
#### I. $\text{Fe}^{+II}$ State (Ferrous)

It is the most stable state of Fe and salts are called ferrous salts. In aqueous solutions, ferrous salts are pale green and contain the  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  ion.

##### (a) Green Vitriol $[\text{FeSO}_4 \cdot 7\text{H}_2\text{O}]$

It is a pale green crystalline solid soluble in water. It is efflorescent and isomorphous with Epsom salt ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) and white vitriol ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ). It is prepared by adding dilute  $\text{H}_2\text{SO}_4$  to iron or to FeS in the kipp's apparatus.





1.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{140^\circ\text{C}} \text{FeSO}_4 \cdot \text{H}_2\text{O} \xrightarrow{300^\circ\text{C}} \text{FeSO}_4 \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + \text{SO}_2 \uparrow + \text{SO}_3 \uparrow$
2.  $\text{FeSO}_4 + (\text{NH}_4)_2\text{SO}_4 + 6\text{H}_2\text{O} \longrightarrow \text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$   
(Mohr's salt)

Mohr's salt is double salt used as a primary standard compound in volumetric analysis for titrations with oxidising agents such as dichromate, permanganate and ceric solutions where  $\text{Fe}^{2+}$  is oxidised to  $\text{Fe}^{3+}$ .

3.  $\text{FeSO}_4 + 2\text{KCN} \longrightarrow \text{Fe}(\text{CN})_2 + \text{K}_2\text{SO}_4$   
 $\text{Fe}(\text{CN})_2 + 4\text{KCN} \longrightarrow \text{K}_4[\text{Fe}(\text{CN})_6]$   
Potassium ferrocyanide
4.  $\text{FeSO}_4$  and  $\text{H}_2\text{O}_2$  are used as Fenton's reagent for producing hydroxyl radicals, for example oxidising alcohols to aldehydes.

#### (b) FeO

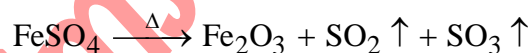
It is a non stoichiometric, metals deficient compound more precisely written as  $\text{Fe}_{0.95}\text{O}$ . It dissolves in acids and is completely basic.

## II. $\text{Fe}^{\text{III}}$ State (Ferric)

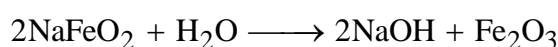
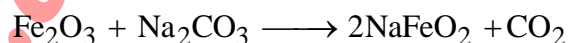
It is a very important oxidation state. Salts are often called ferric salts and solution are usually yellow brown. The colour is due to the presence of colloidal iron oxide ( $\text{FeO} \cdot \text{OH}$ )

#### (a) Ferric Oxide ( $\text{Fe}_2\text{O}_3$ )

It is also a non stoichiometric red - brown compound prepared in the laboratory by strongly heating  $\text{FeSO}_4$ .

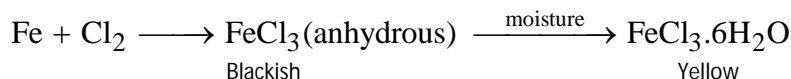


Igniting  $\text{Fe}_2\text{O}_3$  at  $1400^\circ\text{C}$  produces  $\text{Fe}_3\text{O}_4$  or  $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$  (a black solid). It is largely basic and when fused with  $\text{Na}_2\text{CO}_3$  gives ferrites ( $\text{NaFeO}_2$ ). Ferrites hydrolyse with water forming  $\text{NaOH}$ .



**(b) Ferric Chloride (FeCl<sub>3</sub>)**

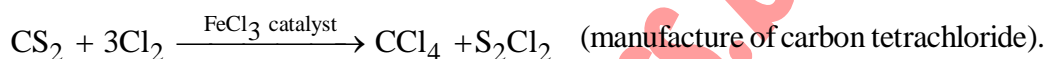
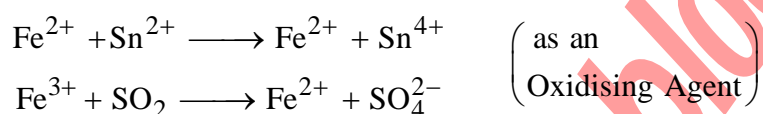
It exists as yellow deliquescent solid FeCl<sub>3</sub> · 6H<sub>2</sub>O. It is very soluble in water, alcohol and ether.



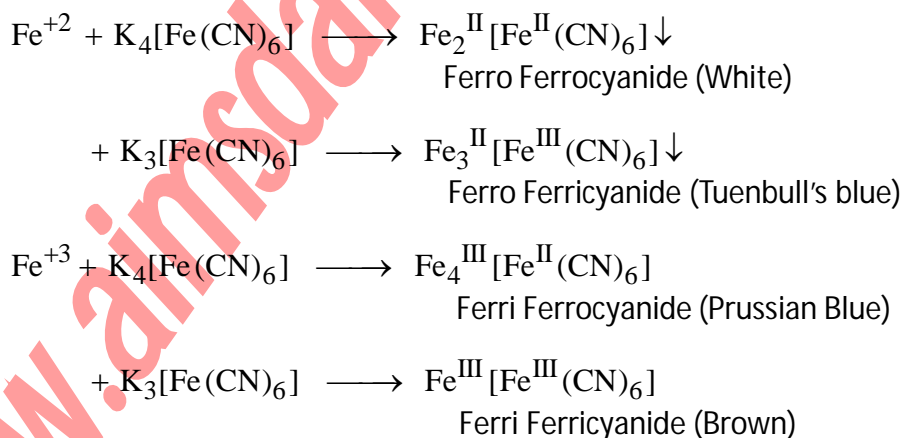
Hydrolysis of FeCl<sub>3</sub> does not produce Fe(OH)<sub>3</sub> but gives a red-brown gelatinous precipitate of the hydrous oxide Fe<sub>2</sub>O<sub>3</sub>(H<sub>2</sub>O)<sub>n</sub>. On heating FeCl<sub>3</sub> at 500°C FeCl<sub>2</sub> and Cl<sub>2</sub> are obtained.

**Uses :**

FeCl<sub>3</sub> is used as an oxidising agent and in the manufacture of CCl<sub>4</sub>.

**Cyanide Complexes**

Iron forms two important complexes with the cyanide ion namely *hexacyanoferrate (II)* {Fe<sup>II</sup>(CN)<sub>6</sub>}<sup>4-</sup> and *hexacyanoferrate(III)* {[Fe<sup>III</sup>(CN)<sub>6</sub>}<sup>3-</sup>}. Hexacyanoferrate(II) is also known as *ferrocyanide ion* while hexacyanoferrate (III) is also known as *ferricyanide ion*. Both these ions form coloured salts with metal ions like K<sup>+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup> which are used in qualitative analysis. Potassium ferrocyanide K<sub>4</sub>[Fe(CN)<sub>6</sub>] is a yellow coloured solid which is famously used to detect Fe<sup>2+</sup> (and Fe<sup>3+</sup>) ions in solution. It forms a white coloured precipitate with Fe(+II) and a Prussian blue solution with Fe(+III) ions. Potassium ferricyanide K<sub>3</sub>[Fe(CN)<sub>6</sub>] can also be used for the same purpose as it gives Turnbull's blue colour with Fe(+II) and a brown colour with Fe(+III). The reactions are :



One of the best tests for Fe(+III) is to add aqueous solutions containing SCN<sup>-</sup> ions. A blood red colour is produced due to a mixture of Fe(SCN)<sub>3</sub> and [Fe(SCN)(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup>.

**[B] Cobalt & Its Compounds**

Cobalt is a very tough metal which resembles iron. It is bluish white and lustrous in appearance. Like iron it is ferromagnetic (Curie temperature =  $1000^{\circ}\text{C}$ ) but relatively unreactive as it does not react with  $\text{H}_2\text{O}$ ,  $\text{H}_2$  or  $\text{N}_2$ . However, it forms the most number of complexes and more compounds than any other element except carbon.

**I.  $\text{Co}^{+II}$  State**

+II state is the most important oxidation state for simple compounds of cobalt. Some compounds in this state are  $\text{CoO}$ ,  $\text{CoCl}_2$ ,  $\text{CoSO}_4$ ,  $\text{CoCO}_3$ . The hydrated salts are all pink or red due to the hexahydrate ion  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  while  $\text{CoO}$  is olive green. Thus  $\text{CoCl}_2$  is used as a test for water and as an indicator added to the drying agent 'silica gel'.  $\text{CoO}$  in combination with  $\text{ZnO}$  is used as a green pigment in paints called Rinnmann's green.

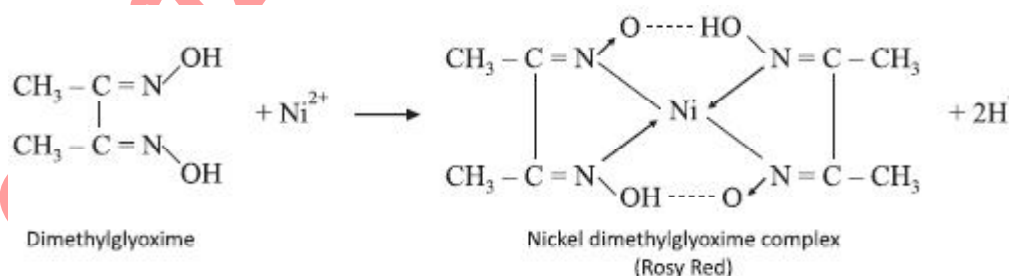
**II.  $\text{Co}^{+III}$  State**

This state is the most important state for complexes of cobalt. Since the (+II) state is common for simple compounds, it is difficult to oxidise  $\text{Co}^{+2}$  to  $\text{Co}^{+3}$  and  $\text{Co}^{+3}$  are less stable and are reduced by water. In contrast many  $\text{Co}(+II)$  complexes are readily oxidised to  $\text{Co}(+III)$  complexes,  $\text{Co}(+III)$  complexes being more stable.

**[C] Nickel & its Compounds**

Nickel, a silvery white metal which does not tarnish in air is produced in large quantities and used in a wide variety of alloys both ferrous and non-ferrous. All three metals ( $\text{Ni}$ ,  $\text{Pd}$ ,  $\text{Pt}$ ) of Group 10, are used as catalysts in many reactions. For example, 'Raney Nickel' is very finely divided nickel used in reduction processes and  $\text{Pd}$  is used for hydrogenation.

Nickel is predominantly divalent in both its simple compounds and complexes. The hydrated salts are bright green coloured due to the hydrated ion  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ . Complexes are commonly square planar or octahedral. The red coloured complex precipitated by  $\text{Ni}^{2+}$  and dimethylglyoxime from slightly ammoniacal solution is square planar. This reaction is used both for detection and quantitative estimation of  $\text{Ni}$ .



## IN-CHAPTER EXERCISE - C

1. Write the chemical reactions associated with the Brown Ring Test.
2. A hydrated metallic salt A, light green in colour, gives a white anhydrous residue B after being heated gradually. B is soluble in water and its aqueous solution reacts with NO to give a dark brown compound C. B on strong heating gives a brown residue D and a mixture of two gases E and F. The gaseous mixture, when passed through acidified  $\text{KMnO}_4$  discharges the pink colour, when passed through acidified  $\text{BaCl}_2$  solution, gives a white precipitate. Identify A, B, C, D, E and F.

NOW ATTEMPT IN-CHAPTER EXERCISE-C REMAINING QUESTIONS IN THIS EBOOK

## COPPER GROUP [COINAGE METALS]

## Section - 5

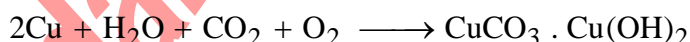
Group 11 consists of the metals copper, gold and silver, all having a completely filled d-shell and one s-electron. They have been known since prehistoric times when they were used to make coins and hence called Coinage Metals. They conduct electricity and heat particularly well and tend to be noble (unreactive). The reason for their noble character is higher ionisation energy and enthalpy of sublimation.

**[A] Copper & its Compounds**

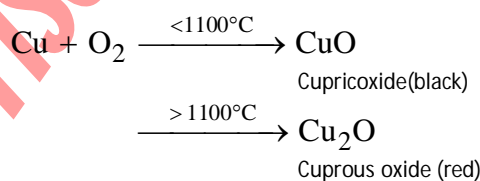
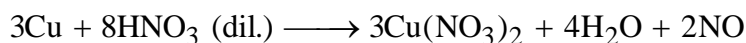
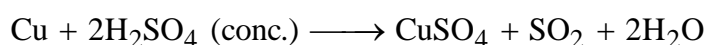
Copper is a reddish coloured, lustrous and soft metal produced on large scale from its ores like chalcopyrite ( $\text{CuFeS}_2$ ), malachite ( $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ ), cuprite ( $\text{Cu}_2\text{O}$ ). The metal is used in the electrical industry because of its high conductivity, electroplating, in manufacture of coins and also as a catalyst.

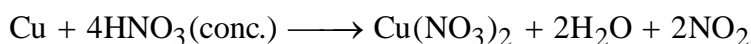
**(i) Reaction with air :**

A green coating of basic copper carbonate  $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$  called 'Verdigris' is formed in presence of moisture and  $\text{CO}_2$  in air ( $\text{O}_2$ ).

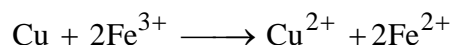
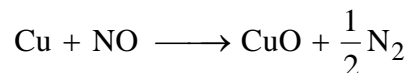


While, when heated it forms two oxides :

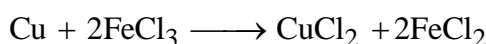
**(ii) Copper is inert towards non-oxidising acids (HCl, dil.  $\text{H}_2\text{SO}_4$ ) but reacts with concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ .**



- (iii) Copper reduces oxides of nitrogen to  $\text{N}_2$  and ferric ion to ferrous ion.

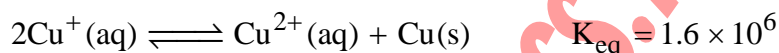


The etching of designs on copper plates using ferric chlorides is based on this property.



### I. $\text{Cu}^{\text{I}}$ State

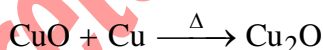
The configuration of copper in (+I) state is  $3d^{10}$  to  $4s^0$  which is known as 'pseudo-noble gas configuration'. It might thus be expected that the (+I) state would be the most stable but surprisingly this is not so. In fact it disproportionates in aqueous solution as :



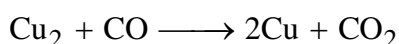
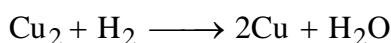
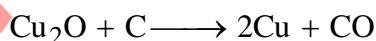
The only  $\text{Cu}^+$  compounds stable in water are either insoluble ( $\text{CuCl}$ ,  $\text{CuBr}$ ,  $\text{CuI}$ ,  $\text{CuCN}$ ) or present as complexes.

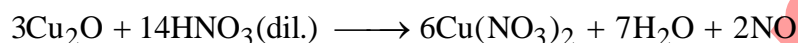
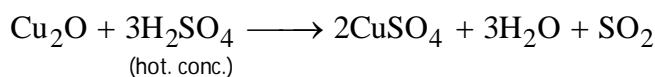
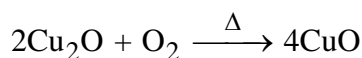
#### (a) Cuprous Oxide ( $\text{Cu}_2\text{O}$ ) :

$\text{Cu}_2\text{O}$  is a red coloured basic oxide found as the ore cuprite in nature. It is prepared by heating cupric oxide and copper or by reduction of  $\text{Cu}^{2+}$  by mild reducing agents (as in the *Fehling's Test* for reducing sugars).

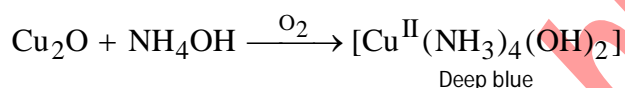
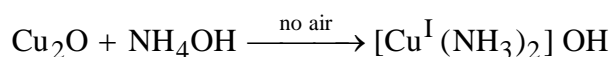


- (i)  $\text{Cu}_2\text{O}$  reacts with halogen acids  $\text{HCl}$ ,  $\text{HBr}$  and  $\text{HI}$  giving insoluble  $\text{CuCl}$ (white),  $\text{CuBr}$ (yellow) and  $\text{CuI}$ (yellow).  $\text{CuF}$  is unknown.
- (ii)  $\text{Cu}_2\text{O}$  is reduced to copper when heated in a current of  $\text{H}_2$  or  $\text{CO}$  or with carbon.



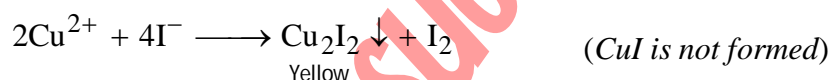
(iii) Oxidation of  $\text{Cu}_2\text{O}$  :

(iv) Reaction with aqueous ammonia :

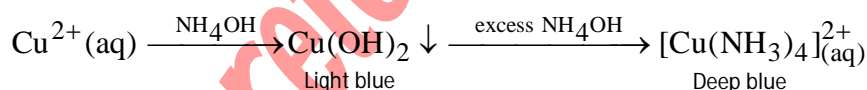


## II. $\text{Cu}^{+II}$ State

It is the most important and stable state of copper. Since the electronic configuration is  $d^9$ , the compounds are typically coloured due to  $d-d$  spectra and paramagnetic. The hydrated salts are blue due to  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ions.  $\text{Cu}^{2+}$  compounds are detected by adding a KI solution which forms yellow precipitate of  $\text{Cu}_2\text{I}_2$ .

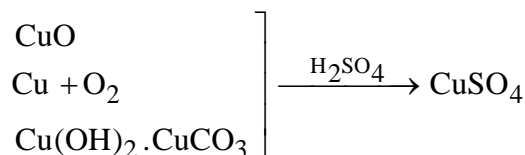


This is also used in the volumetric analysis of  $\text{Cu}^{+II}$ . Another test is adding the salt to  $\text{NH}_4\text{OH}$  solution.

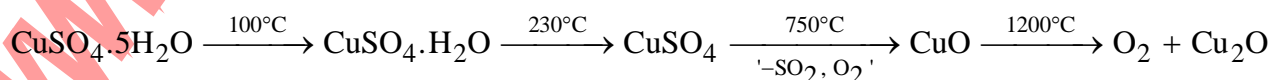
(a) **Copper sulphate  $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$  :**

Also known as blue vitriol, copper sulphate solutions are blue coloured. The anhydrous salt is however white.

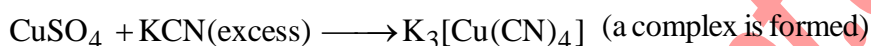
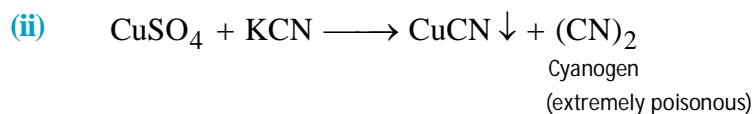
It is prepared by dissolving  $\text{CuCO}_3$ ,  $\text{Cu}(\text{OH})_2$  or  $\text{CuO}$  in sulphuric acid.



(i) Hydrated copper sulphate crystals are blue coloured and thus this can be used as a test for the presence of water on heating, the water of crystallisation is lost.



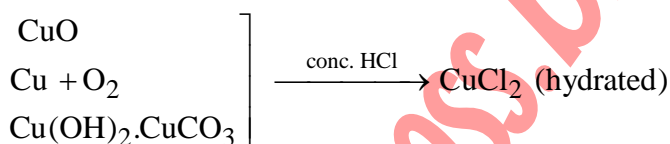




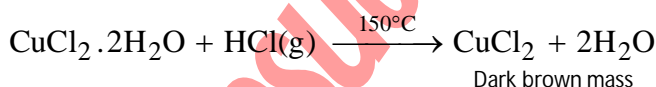
(iii) A mixture of  $\text{CuSO}_4$  and  $\text{Ca(OH)}_2$  (milk lime) is used as *Bordeaux Mixture* used for preventing fungus attack on potato leaves and vines.  $\text{CuSO}_4$  is also used to make fehling solution.

(b) Cupric Chloride  $[\text{CuCl}_2 \cdot 2\text{H}_2\text{O}]$  :

Cupric chloride can be obtained by dissolving  $\text{Cu}(\text{OH})_2$ ,  $\text{CuCO}_3$  or  $\text{CuO}$  or the metal in conc.  $\text{HCl}$ .

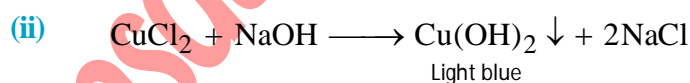


The hydrated crystals are green coloured. Anhydrous salt can be obtained by heating in HCl gas.



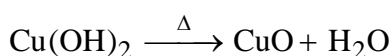
(i) It is a deliquescent compound readily soluble in water. Dilute solutions are blue while concentrated solutions are green. It changes to yellow if added to conc.  $\text{HCl}$  or  $\text{Cl}_2$  current is passed.

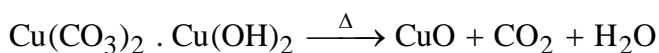
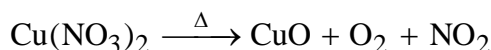
The blue colour is due to  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  and yellow colour due to complex ion  $[\text{CuCl}_4]^{2-}$



(c) **Cupric Oxide [CuO] :**

It is black coloured and formed by heating cuprous oxide or copper in air ( $O_2$ ). In fact, all oxosalts, such as  $Cu(NO_3)_2$ , decompose into black  $CuO$  on strong heating.

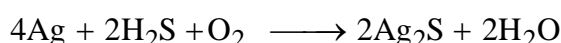




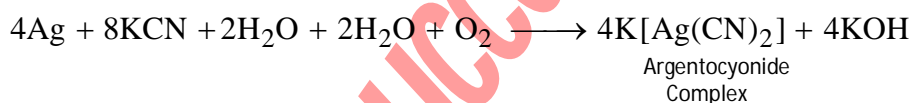
## [B] Silver & its Compounds

Silver is a white lustrous, ductile and malleable metal. It is the best known conductor of electricity and heat. The chemical properties of silver are :

- (i) It is quite unreactive and has no effect of air and alkalies. However, air contaminated with  $\text{H}_2\text{S}$  tarnishes silver due to formation of black  $\text{Ag}_2\text{S}$ .



- (ii) On heating the molten mass of silver absorbs oxygen which is again released on cooling. This is called as 'SPITTING OF SILVER'.
- (iii) Ag dissolves in conc.  $\text{HNO}_3$  and conc.  $\text{H}_2\text{SO}_4$  producing  $\text{NO}_2$  and  $\text{SO}_2$  respectively. Dilute  $\text{H}_2\text{SO}_4$  has no effect on silver but dilute  $\text{HNO}_3$  react to form  $\text{NO}$  (Ag being a poor reducing agent). In each case Ag is oxidised to  $\text{Ag}^+$  ion.
- (iv) Cyanide complexes are used in the extraction of silver.

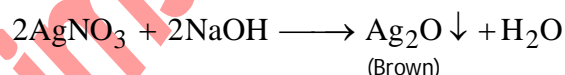


- (v) Silver finds its use as  $\text{AgCl}$  and  $\text{AgBr}$  in photographic emulsions. Other uses include in making jewellery and ornaments, silver mirrors and for batteries.

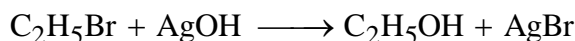
The most stable and common oxidation state of silver is the (+I) state. Some compounds in this state are :

### (a) Silver oxide [ $\text{Ag}_2\text{O}$ ] :

$\text{Ag}_2\text{O}$  is mainly basic and prepared from silver salts like  $\text{AgNO}_3$



- (i) On heating silver oxide decomposes to silver and oxygen at  $160^\circ\text{C}$ .
- (ii) Aqueous solutions of  $\text{Ag}_2\text{O}$  consist of  $\text{Ag}(\text{OH})$  making the solution strongly basic. Thus the moist  $\text{Ag}_2\text{O}$  can hydrolyse alkyl halides.

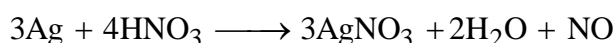


Moist  $\text{Ag}_2\text{O}$  also absorbs carbon dioxide and forms  $\text{Ag}_2\text{CO}_3$ .

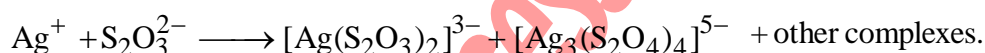
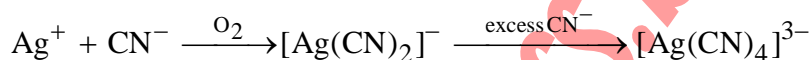
3.  $\text{Ag}_2\text{O}$  forms black coloured  $\text{AgO}$  with sodium thiosulphate. This oxide actually exists as  $\text{Ag}^{\text{I}}[\text{Ag}^{\text{III}}\text{O}_2]$  and hence is diamagnetic not paramagnetic.

**(b) Silver Nitrate [ $\text{AgNO}_3$ ] (Lunar Caustic) :**

Silver nitrate is one of the most important salts of silver. It can be formed by simply dissolving Ag in nitric acid.



1. In crystalline form it is colourless. Heating  $\text{AgNO}_3$  dissociates it into Ag,  $\text{NO}_2$  and  $\text{O}_2$ .
2. All simple compounds of  $\text{Ag}^+$  ( $\text{Ag}_2\text{O}$ ,  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgNO}_3$ ) form complexes with alkali cyanide and sodium thiosulphate.



3. A solution of  $\text{AgNO}_3$  and alkaline aqueous ammonia is used as *Tollens Reagent* (ammoniacal  $\text{AgNO}_3$  or  $[\text{Ag}(\text{NH}_3)_2]\text{OH}^-$ )

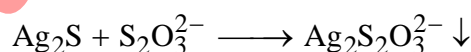


**(c) Silver Halides :**

Silver halides ( $\text{AgX}$ ) are insoluble solids used in photography.  $\text{AgCl}$  is white,  $\text{AgBr}$  pale yellow and  $\text{AgI}$  yellow. Presence of halide ions in solutions is tested by adding  $\text{AgNO}_3$  solution and dil.  $\text{HNO}_3$  which forms silver halide precipitates. The colour indicates the type of halide ion present. This can be confirmed by testing solubility of these precipitates in ammonium hydroxide.  $\text{AgCl}$  is soluble in dilute  $\text{NH}_4\text{OH}$ .  $\text{AgBr}$  fully dissolves only in strong ammonia solution while  $\text{AgI}$  is insoluble in  $\text{NH}_4\text{OH}$ . ( $\text{AgCl}$  and  $\text{AgBr}$  form the soluble ammine complex  $\text{Ag}(\text{NH}_3)_2^+$  which is linear).

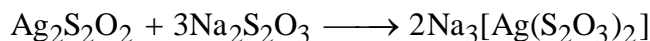
**(d) Silver thiosulphate [ $\text{Ag}_2\text{S}_2\text{O}_3$ ] :**

It forms white needle like crystals precipitated when  $\text{Ag}_2\text{S}$  or  $\text{AgNO}_3$  reacts with hypo.

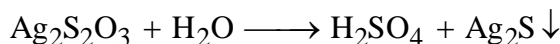


White

On adding excess of sodium thiosulphate, it dissolves.

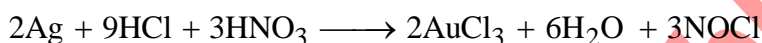


- $\text{Ag}_2\text{S}_2\text{O}_3$  is decomposed by water giving a variety of colours changing from black through yellow and brown.



### [C] Gold

Gold(Au) is a soft, heavy and yellow metal with high lustre. It is inert to air and all acids except aqua regia (a 3 : 1 mixture of concentrated HCl and  $\text{HNO}_3$ ). The  $\text{HNO}_3$  acts as an oxidising agent and the chloride ions as a complexing agent.



The most stable oxidation state for gold is Au(+III)

### IN-CHAPTER EXERCISE - D

1. Explain the following facts :

- (i) Silver nitrate is kept in dark coloured bottles :
- (ii) Copper hydroxide is soluble in ammonium hydroxide but not in sodium hydroxide.
- (iii) Cuprous chloride is insoluble in water and dilute HCl but dissolves in concentrated HCl.
- (iv) The species  $[\text{CuCl}_4]^{2-}$  exists but  $[\text{CuI}_4]^{2-}$  does not .
- (v) Addition of an alkali to cuprous chloride solution gives a yellow precipitate which gradually changes to a red colour.

NOW ATTEMPT IN-CHAPTER EXERCISE-D REMAINING QUESTIONS IN THIS EBOOK

## ZINC GROUP - GROUP 12

## Section - 6

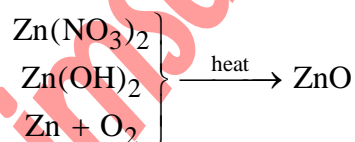
The elements of group 12 have a  $d^{10}s^2$  configuration and they typically form divalent ions. Since they have a fully filled orbital in native as well as any other state, they do not behave as typical transition metals (like they are very soft).

The members of this group are zinc (Zn), cadmium (Cd) and mercury (Hg).

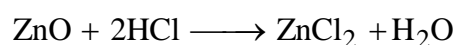
## Zinc &amp; its Compounds

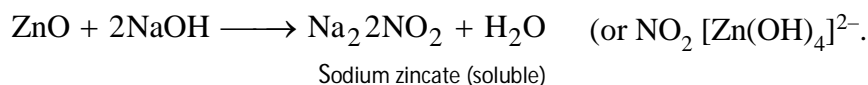
Zinc is bluish white crystalline metal which shows some similarities to Mg. It is brittle at ordinary temperature, malleable and ductile at  $100^\circ - 150^\circ \text{C}$  and again becomes brittle at  $220^\circ \text{C}$ . Some properties are :

- $2\text{Zn} + \text{O}_2 \xrightarrow{\Delta} 2\text{ZnO}$
- $\text{Zn}(\text{red hot}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{ZnO} + \text{H}_2$
- Reaction with acids :
  - $\text{Zn} + 2\text{H}_2\text{SO}_4(\text{conc.}) \longrightarrow \text{ZnSO}_4 + \text{H}_2\text{O} + \text{SO}_2$
  - $4\text{Zn} + 10\text{HNO}_3(\text{very dil.}) \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$
  - $3\text{Zn} + 8\text{HNO}_3(\text{moderately conc.}) \longrightarrow 3\text{Zn}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
  - $\text{Zn} + 4\text{HNO}_3(\text{hot conc.}) \longrightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
- Reaction with NaOH :  $\text{Zn} + 2\text{NaOH}(\text{hot}) \longrightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2$   
Sodium zincate(soluble)
- Uses :** Zinc is used in larger amounts for coating iron to prevent it from rusting, make alloys (brass is Zn + Cu), sheets used for roofing and as a reducing agent. It also has an important role in biological systems.
- (a) Zinc oxide (ZnO) :** ZnO is a white, light powder insoluble in water and made by heating zinc salts.



- ZnO is white when cold and becomes yellow on heating. The colour occurs due to loss of O atoms on heating, creating defects in structure.
- ZnO is amphoteric. In acids it forms salts and in alkali, zincates such as  $[\text{Zn}(\text{OH})_4]^{2-}$ .

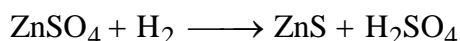




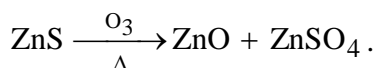
3. ZnO is the only important commercial oxide in this group. It is used mainly in vulcanization of rubber. It is also used as white shoe polish and manufacture of glass.

### (b) Zinc Sulphide (ZnS) :

ZnS is also white and insoluble in water. It turns yellow on exposure to light. Zinc oxide or zinc sulphate or other zinc salts form zinc sulphide in the presence of  $\text{H}_2\text{S}$  gas.

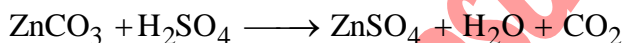


1. It shows phosphorescence due to impurities of Mn, Cu, Ag etc. and hence is used as a phosphorescent.
2. On heating in oxygen at high temperature ZnO is formed while  $\text{ZnSO}_4$  is the major product at low temperature.



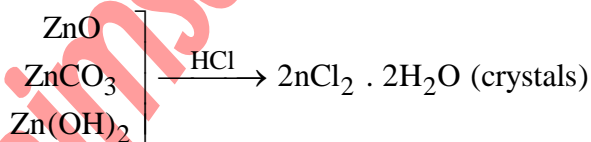
### (c) Zinc Sulphate [ $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ] (White vitriol) :

White vitriol is isomorphous with epsom salts and green vitriol. It is highly soluble in water and prepared as follows:



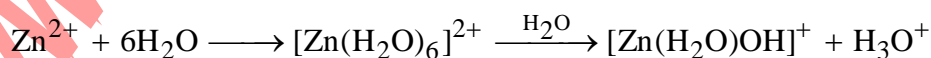
1.  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{100^\circ\text{C}} \text{ZnSO}_4 \cdot 6\text{H}_2\text{O} \xrightarrow{280^\circ\text{C}} \text{ZnSO}_4 \xrightarrow{800^\circ\text{C}} \text{ZnO} + \text{SO}_2 + \text{O}_2$
2. It is used in medicine as an eye lotion and in manufacture of white point.

### (d) Zinc Chloride ( $\text{ZnCl}_2$ ) : It is a white deliquescent solid very soluble in water.



Heating hydrated  $\text{ZnCl}_2$  simply decomposes it to ZnO instead of dehydrating to anhydrous form.

1. Aqueous solutions of  $\text{Zn}^{2+}$  are acidic because of hydrolysis.





2.  $\text{ZnCl}_2 + \text{H}_2\text{S} \longrightarrow \text{ZnS} \downarrow + 2\text{HCl}$
3.  $\text{ZnCl}_2 \xrightarrow{\text{NaOH}} \text{Zn(OH)} \downarrow \text{(White gelatinous precipitate)} \xrightarrow{\text{NaOH}} \text{Na}_2\text{ZnO}_2$   
Sodium zincate
4. (i)  $\text{ZnCl}_2 \xrightarrow{\text{NH}_4\text{OH}} \text{Zn(OH)}_2 \downarrow \xrightarrow{\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}} [\text{Zn(NH}_3)_4]\text{Cl}_2$   
Tetramminezinc Chloride
- (ii)  $\text{ZnCl}_2 \xrightarrow{4\text{NH}_3} \text{ZnCl}_2 \cdot 4\text{NH}_3$
5. Concentrated solutions of zinc chloride are corrosive and dissolve paper. It is used for treating textiles.  $\text{ZnCl}_2$  is also used as a flux for soldering.

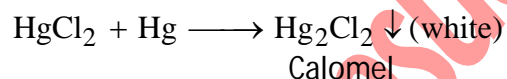
### Mercury & its Compounds

Mercury is a silvery liquid which does not tarnish readily. All mercury (and cadmium) compounds are toxic. It has two oxidation states +I and +II. Hg(I) compounds (*mercurous* compounds) are few in number and contain the ion  $(\text{Hg} - \text{Hg})^{2+}$  and  $\text{Hg}^+$ . Hg(II) compounds (*mercuric* compounds) are more covalent and stable.

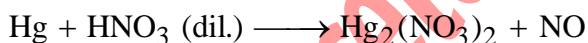
Hg is used in thermometers, barometers and mercury vapour street lights.

#### I. $\text{Hg}^{\text{+I}}$ State (Mercurous)

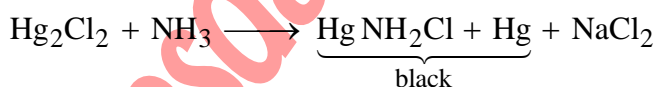
Mercurous compound can be made by reducing the Hg(II) salts with the metal.



Alternatively, mercury (I) nitrate can be made by dissolving Hg in dilute  $\text{HNO}_3$ .

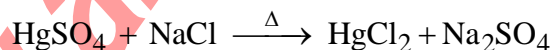


- $\text{Hg}_2\text{Cl}_2$  also known as calomel is used in calomel electrodes. It is a white powder which turns black in  $\text{NH}_3$  (which is used in detection of mercurous ion).

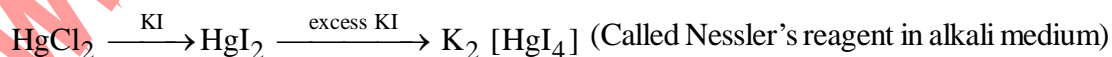


#### II. $\text{Hg}^{\text{+II}}$ State (Mercuric)

Salts are usually anhydrous. Mercuric chloride ( $\text{HgCl}_2$ ) is called 'Corrosive Sublimate' and prepared as follows:



It is a colourless crystalline highly poisonous solid used as an antiseptic since the middle Ages. It is also used to make *Nessler's Reagent* which is used to detect  $\text{NH}_3$ .



## IN-CHAPTER EXERCISE - E

1. Write balanced equations for the reaction of alkaline perbromate with zinc giving tetrahydroxozincate anion.
2. Excess of dilute sodium hydroxide solution is gradually added with shaking to an aqueous solution of zinc sulphate. What would you observe?
3. Explain the following:
  - (i) The addition of NaOH solution to a solution of zinc chloride produces a white precipitate which dissolves on further addition of NaOH.
  - (ii) The addition of  $\text{NH}_4\text{OH}$  to  $\text{ZnSO}_4$  solution produces white precipitate but no precipitate is formed if it contains  $\text{NH}_4\text{Cl}$ .
4. Mercurous chloride turns black on adding  $\text{NH}_4\text{OH}$  to it. Explain.
5. A white substance A reacts with dilute  $\text{H}_2\text{SO}_4$  to produce a colourless gas B and a colourless solution C. The reaction between B and acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution produces a green solution and a slightly coloured precipitate D. The substance D burns in air to produce a gas E which reacts with B to yield D and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous  $\text{NH}_3$  or NaOH to C produces first a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case. Identify A, B, C, D and E. Write the equations of the reactions involved.

## SOLUTIONS - IN - CHAPTER EXERCISE - A

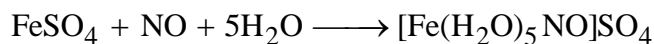
- Due to lanthanoid contraction, the difference between the radius of second and third group elements is negligible. As a result, they have similar lattice energies, solvation energies, ionization energies and other properties.
- Many transition metals contain partially filled electrons shell. The unpaired electrons produce spin magnetic moments which result into paramagnetism.
  - Colour arises from the ability of a compound to absorb particular wavelengths of white light and emit the rest. This can occur when their is/are electrons / charge which can be transferred from an energy level to another which is the case with transition elements and their compounds.

## SOLUTIONS - IN - CHAPTER EXERCISE - B

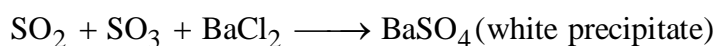
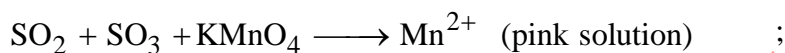
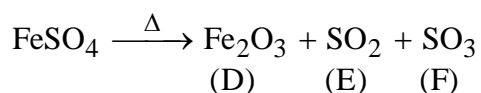
- $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{KI} + 4\text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O} + \text{I}_2$
  - $\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{K}_2\text{CrO}_4 + \text{Cr}_2\text{O}_3 + \text{O}_2$
  - $2\text{KMnO}_4 \xrightarrow{\Delta} \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$  (disproportionation)
  - $2\text{MnO}_4^- + 5\text{AsO}_3^- + 6\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 5\text{AsO}_4^{3-}$
  - $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NH}_4\text{Cl} \longrightarrow (\text{NH}_4)_2\text{Cr}_2\text{O}_7 + 2\text{KCl}$   
 $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \underset{\text{(green)}}{\text{Cr}_2\text{O}_3} + \underset{\text{(gas)}}{\text{N}_2} + 4\text{H}_2\text{O} \quad ; \quad \text{Cr}_2\text{O}_3 + 2\text{Al} \xrightarrow{\Delta} \underset{\text{(metal)}}{2\text{Cr}} + \underset{\text{(oxide)}}{\text{Al}_2\text{O}_3}$
- X is  $\text{NH}_4\text{Cl}$ .  
 $4\text{Cl}^- + \text{K}_2\text{Cr}_2\text{O}_7 + 6\text{H}_2\text{SO}_4 \longrightarrow 2\text{CrO}_2\text{Cl}_2 + 2\text{KHSO}_4 + 4\text{HSO}_4^- + 3\text{H}_2\text{O}$   
 (from  $\text{NH}_4\text{Cl}$ ) (gas A)  
 $\text{CrO}_2\text{Cl}_2 + 4\text{NaOH} \longrightarrow \text{Na}_2\text{CrO}_4 + 2\text{NaCl} + 2\text{H}_2\text{O}$   
 (B)  
 $\text{Na}_2\text{CrO}_4 + (\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow \text{PbCrO}_4 \downarrow + 2\text{CH}_3\text{COONa}$   
 (C)  
 $\text{NH}_4^+ + \text{NaOH} \xrightarrow{\Delta} \text{NH}_3 + \text{Na}^+ + \text{H}_2\text{O}$   
 (From  $\text{NH}_4\text{Cl}$ ) (gas)  
 $\text{NH}_3 + 2\text{HgI}_4^{2-} + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{N}-\text{Hg}-\text{O}-\text{Hg}-\text{I} \downarrow + 7\text{I}^- + 3\text{H}^+$   
 (D)
- The process described is that of preparation of potassium permanganate from pyrolusite ore.  
 $2\text{MnO}_2 + 4\text{KOH} + 2[\text{O}] \xrightarrow{\Delta} 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O} ; 2\text{K}_2\text{MnO}_4 + \text{Cl}_2 \longrightarrow 2\text{KMnO}_4 + 2\text{KCl}$
- $\text{Cr}_2\text{O}_7^{2-} + 3\text{S}^{2-} + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 3\text{S} + 7\text{H}_2\text{O}$

## SOLUTIONS - IN - CHAPTER EXERCISE - C

1. Nitrates produce NO which coordinates with  $\text{Fe}^{2+}$  to give a brown ring.



2.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{\Delta} \text{FeSO}_4 \text{ (white)} \quad ; \quad \text{FeSO}_4 + \text{NO} \xrightarrow{\text{H}_2\text{O}} [\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$   
 (A) (B) (C)



## SOLUTIONS - IN - CHAPTER EXERCISE - D

1. (i)  $\text{AgNO}_3$  decomposes to  $\text{Ag}_2\text{O}$  and  $\text{NO}_2$  in presence of slight heat (due to light) and is thus kept in dark bottles.  
 (ii) This is because  $\text{Cu}^{2+}$  can form many complexes with  $\text{NH}_4^+$  which are soluble in water.  
 (iii) Cuprous halides form soluble complexes in presence of excess of halide ions in solution.



- (iv)  $\text{I}^-$  ion is a stronger reducing agent than  $\text{Cl}^-$  ion. It reduces  $\text{Cu}^{2+}$  ion into  $\text{Cu}^+$  ion. Hence, cupric iodide is converted into cuprous iodide. Thus the species  $[\text{CuI}_4]^{2-}$  does not exist.



Precipitate changes colour from yellow to red due to formation of  $\text{Cu}_2\text{O}$

## SOLUTIONS - IN - CHAPTER EXERCISE - E

- $$\text{BrO}_4^- + \text{Zn} + 2\text{OH}^- + \text{H}_2\text{O} \longrightarrow \text{BrO}_3^- + \text{Zn}(\text{OH})_4^{2-}$$
- $$\text{ZnSO}_4 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SO}_4 + \underset{\text{(white)}}{\text{Zn}(\text{OH})_2} \downarrow \xrightarrow{\text{NaOH}} \underset{\substack{\text{soluble} \\ \text{and} \\ \text{colourless}}}{\text{Na}_2\text{ZnO}_2}$$
- (i) First a white precipitate of  $\text{Zn}(\text{OH})_2$  is formed which on further addition of  $\text{NaOH}$  forms soluble zincate  $\text{Na}_2\text{ZnO}_2$ .

(ii)  $\text{NH}_4\text{OH}$  is a weak hydroxide. It is ionized slightly furnishing  $\text{OH}^-$  ions which are sufficient to precipitate  $\text{Zn}(\text{OH})_2$  because its low solubility product. However, in presence of  $\text{NH}_4\text{Cl}$ , the ionization of  $\text{NH}_4\text{OH}$  is further suppressed and sufficient  $\text{OH}^-$  are not available to cause precipitation.
- $$\text{Hg}_2\text{Cl}_2 + \text{NH}_4\text{OH} \longrightarrow \underbrace{\text{Hg} - \text{NH}_2\text{Cl} + \text{Hg}}_{\text{black}} \quad \text{This is used to detect mercurous ions.}$$
- $$\text{ZnS} + \text{dil. H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{S} + \text{ZnSO}_4 \quad ;$$

(A) (B) (C)

$$3\text{H}_2\text{S} + \text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 3\text{S} + 7\text{H}_2\text{O}$$

(green) (D)

$$\text{S} + \text{O}_2 \longrightarrow \text{SO}_2 \text{ (E)} \quad ; \quad \text{SO}_2 + \text{H}_2\text{S} \longrightarrow \text{S} + \text{H}_2\text{O}$$

(E) (B) (D) (colourless liquid)

$$\text{Zn}^{2+} + 2\text{OH}^- \longrightarrow \text{Zn}(\text{OH})_2 \downarrow \xrightarrow{\text{OH}^-} \text{Zn}(\text{OH})_4^{2-} \text{ (clear solution)}$$

(C)

## My Chapter Notes



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