

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°C for Fe.

Iron is passivated by strong oxidising agents like conc. HNO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ due to the formation of a protective coat of oxide (Fe_2O_3) while with dilute acids Fe is oxidised to Fe^{2+} . Finely divided iron combines with the ligand CO forming $[\text{Fe}(\text{CO})_5]$ which is liquid at room temperature.

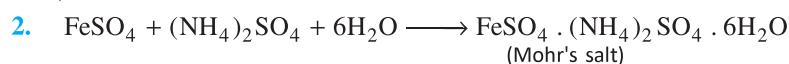
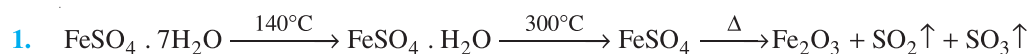
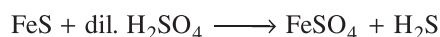
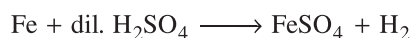
Rusting of iron is a special case of corrosion and is of great importance. Rusting occurs in the presence of O_2 , H_2O and H^+ due to the formation of an oxide film of Fe_2O_3 which is not protective and the corrosion continues. To prevent corrosion, O_2 and H_2O must be excluded. This is done by electroplating 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. Fe^{II} State (Ferrous)

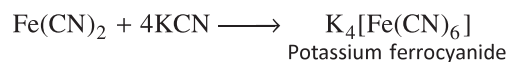
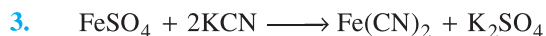
It is the most stable state of Fe and salts are called ferrous salts. In aqueous solutions, ferrous salts are pale green and contain the $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ion.

(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 H_2SO_4 to iron or to FeS in the kipp's apparatus.



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 Fe^{2+} is oxidised to Fe^{3+} .



4. FeSO_4 and H_2O_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. Fe^{+III} State (Ferric)

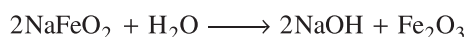
It is a very important oxidation state. Salts are often called ferric salts and solution are usually yellow brown. The colour is due to the presence of colloidal iron oxide ($\text{FeO} \cdot \text{OH}$)

(a) Ferric Oxide (Fe_2O_3)

It is also a non stoichiometric red - brown compound prepared in the laboratory by strongly heating FeSO_4 .

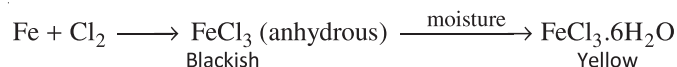


Igniting Fe_2O_3 at 1400°C produces Fe_3O_4 or $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$ (a black solid). It is largely basic and when fused with Na_2CO_3 gives ferrites (NaFeO_2). Ferrites hydrolyse with water forming NaOH .



(b) Ferric Chloride (FeCl_3)

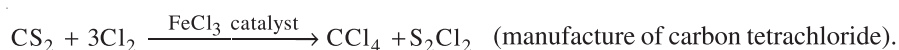
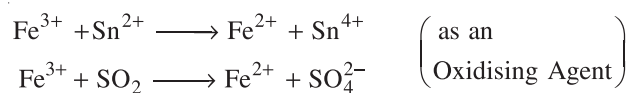
It exists as yellow deliquescent solid $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. It is very soluble in water, alcohol and ether.



Hydrolysis of FeCl_3 does not produce Fe(OH)_3 but gives a red-brown gelatinous precipitate of the hydrous oxide $\text{Fe}_2\text{O}_3(\text{H}_2\text{O})_n$. On heating FeCl_3 at 500°C FeCl_2 and Cl_2 are obtained.

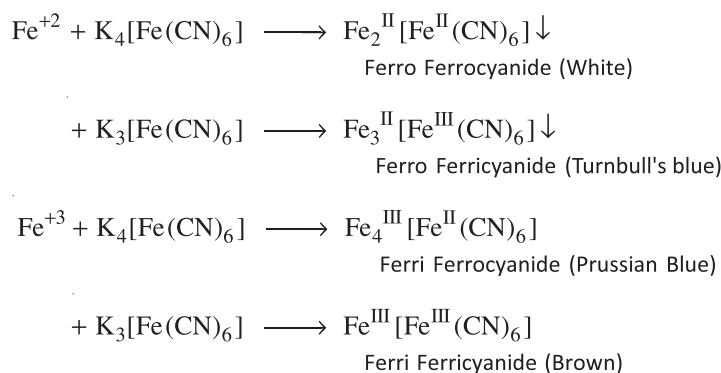
Uses :

FeCl_3 is used as an oxidising agent and in the manufacture of CCl_4 .



Cyanide Complexes

Iron forms two important complexes with the cyanide ion namely *hexacyanoferrate(II)* $\{\text{Fe}^{\text{II}}(\text{CN})_6\}^{4-}$ and *hexacyanoferrate(III)* $\{\text{Fe}^{\text{III}}(\text{CN})_6\}^{3-}$. 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^+ , Cu^{2+} , Fe^{2+} which are used in qualitative analysis. Potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$ is a yellow coloured solid which is famously used to detect Fe^{2+} (and Fe^{3+}) ions in solution. It forms a white coloured precipitate with $\text{Fe}(\text{+II})$ and a Prussian blue solution with $\text{Fe}(\text{+III})$ ions. Potassium ferricyanide $\text{K}_3[\text{Fe}(\text{CN})_6]$ can also be used for the same purpose as it gives Turnbull's blue colour with $\text{Fe}(\text{+II})$ and a brown colour with $\text{Fe}(\text{+III})$. The reactions are :



One of the best tests for $\text{Fe}(\text{+III})$ is to add aqueous solutions containing SCN^- ions. A blood red colour is produced due to a mixture of $\text{Fe}(\text{SCN})_3$ and $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$.

[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°C) but relatively unreactive as it does not react with H_2O , H_2 or N_2 . However, it forms the most number of complexes and more compounds than any other element except carbon.

I. Co^{+II} State

+II state is the most important oxidation state for simple compounds of cobalt. Some compounds in this state are CoO , CoCl_2 , CoSO_4 , 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 CoO is olive green. Thus CoCl_2 is used as a test for water and as an indicator added to the drying agent 'silica gel'. CoO in combination with ZnO is used as a green pigment in paints called Rinnmann's green.

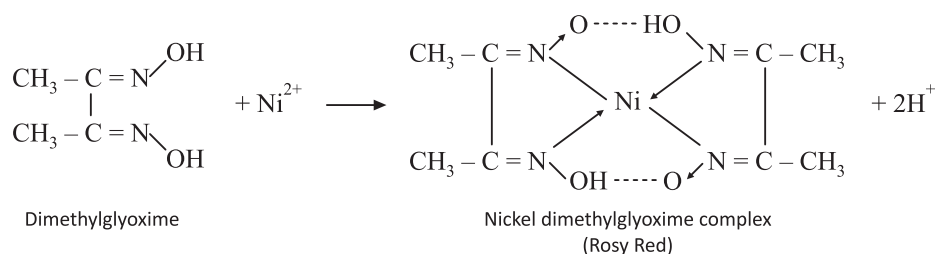
II. Co^{+III} State

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 Co^{+2} to Co^{+3} and Co^{+3} are less stable and are reduced by water. In contrast many $\text{Co}(\text{+II})$ complexes are readily oxidised to $\text{Co}(\text{+III})$ complexes, $\text{Co}(\text{+III})$ 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 (Ni, Pd, 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 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 Ni^{2+} and dimethylglyoxime from slightly ammoniacal solution is square planar. This reaction is used both for detection and quantitative estimation of 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 KMnO_4 discharges the pink colour, when passed through acidified BaCl_2 solution, gives a white precipitate. Identify A, B, C, D, E and F.

Choose the correct alternative. Only One choice is Correct.

- *3.** Which of the following statement(s) is(are) correct with reference to the ferrous and ferric ions ?
- (A) Fe^{3+} gives brown color with potassium ferricyanide
 - (B) Fe^{2+} gives blue precipitate with potassium ferricyanide
 - (C) Fe^{3+} gives red color with potassium thiocyanate
 - (D) Fe^{2+} gives brown color with ammonium thiocyanate
- *4.** Which of the following statements is correct ?
- (A) Nickel is a silver white metal
 - (B) Nickel dimethylglyoxime is square planar
 - (C) Among complexes of cobalt the most stable are those of Co^{+2}
 - (D) Among simple compounds of cobalt the most stable are those of Co^{+2}