Sem-IV.

~~[illegible]~~ ~~[illegible]~~ d-block

08 **Iron (Fe)** ⇒ Electronic configuration := [Ar] $3d^6 4s^2$

09 Oxidation state :=

The main oxidation states of iron
10 is (+II) and (+III).

The highest oxidation state of
11 Fe should be +VIII ~~having~~ by using all valance electrons but the maximum oxidation state of
12 ~~ion~~ iron is (+VI) which is rare and less important.

01 Stability of (+II) and (+III) ⇒

02 (+III) state is more stable than (+II)
03 state due to the ~~d^6~~ ~~[illegible]~~ ~~configuration~~ ~~so~~ d^5 ~~electronic~~ ~~distri~~ configuration.

04 It forms mainly high spin complex due to $t_{2g}^3 e_g^2$ configuration.

05

06

General ~~Gen~~ Properties :=

Iron forms Fe(II) when reacts with non-oxidising acids like HCl.

Iron form Fe(III) when reacts with oxidising acids like HNO_3.

Iron forms both Fe(II) and Fe(III) when non-oxidising

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acid is warm and air is present. Actually the Fe(II) formed are oxidised to Fe(III) thus we get a mixture of Fe(II) and Fe(III).

It forms hydroxide when reacts with concentrated NaOH soln.

As Fe reacts with both acids and bases, it is amphoteric in nature.

Iron is pyrophoric in nature, as it continuously reacts with oxygen of moist air and forms a flaky layer of iron oxide.

+II oxdn state

It is a stable oxidation state of iron. It forms $[Fe(H_2O)_6]^{2+}$ complex ion is aqueous solution. It is difficult to crystalize it as it readily oxidises to +III state. But, in double salt, Mohr's salt, it is stable.

(FeO) The oxide of Fe(II) is non-stoichiometric and is metal deficient. The oxide is completely basic and dissolves in acids.

The halides are formed when the iron dissolves in halogen acids in absence of air. It gives hydrated dihalides.

$$Fe + \underset{\text{soln.}}{HX} \longrightarrow FeX_2 \text{ (hydrated)}$$

$$Fe + HX(g) \xrightarrow{\text{heat}} FeX_2 \text{ (anhyd.)}$$

$(X = F, Cl)$

08 $FeX_2 \cdot xH_2O \xrightarrow{heat} FeX_2 + xH_2O\,(g)$

(X = Br, I)

09

10 The anhyd. FeX_2 reacts with gaseous NH_3, forming salts having $[Fe(NH_3)_6]^{2+}$ complex ion which decomposes in water to form $Fe(OH)_2$.

11

$$FeX_2\,(anhyd.) + NH_3\,(g) \longrightarrow [Fe(NH_3)_6]^{2+}$$

12 $\downarrow H_2O$

01 $Fe(OH)_2 + Fe(OH)_3 \xleftarrow[\text{air}]{O_2 \text{ in}} Fe(OH)_2 \downarrow$

(dark green) white solid

02 $\downarrow$ O_2 in air

03 $Fe_2O_3 \cdot (H_2O)_n$

04 (brown)

05 (*) The colours of Fe(II) halides intensifies ~~on~~ ~~going~~ ~~down~~ with increasing size of the halide

06 ions. ~~due~~ ~~to~~ ~~increase~~ ~~in~~ for a same cation, with increasing the size of anions polarizabili increases, covalent character increases, colour intensifie

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Complex Formation :-

The well known complex of Fe(II) is Potassium hexacyanoferrate(II) or potassium ferrocyanide, $K_4[Fe(CN)_6]$, yellow in colour.

It is used to detect the presence of Fe^{3+} in solution. If Fe^{3+} is present, then it gives a intense blue coloured solution known as Prussian Blue.

$$K_4[Fe(CN)_6] + Fe^{3+} \longrightarrow K\,Fe^{III}[Fe^{II}(CN)_6] \downarrow$$

(Prussian blue)

If the solution contains Fe^{2+} then it forms a white precipitate.

$$K_4[Fe(CN)_6] + Fe^{2+} \longrightarrow K_2Fe^{II}[Fe^{II}(CN)_6] \downarrow$$

(white ppt.)

The intense colour of ~~pru~~ Prussian blue is due to the charge transfer or electron transfer between Fe(II) and Fe(III) which is not possible in case of the complex with Fe(II).

Fe(II) is a good π-donor as compared to Fe^{3+} thus π-acceptor ligands like o-phenanthroline form stable complexes with Fe^{2+}. The complex of tris-(o-phenanthroline) Iron(II) sulphate is widely used as redox indicator and well know as ferroin. It changes the colour sharply from deep red to ~~deep~~ pale blue on oxidation.

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The lost child

Fe(II) ~~very~~ ~~is~~ has an important biological role as it present in haemoglobin (O_2 transport), myoglobin (O_2 storage),

Sodium nitroprusside is another important complex of Fe(II) which is formed by replacing one CN^- of ferrocyanide ion with NO^+. It is used in qualitative ~~a~~ analysis of sulphide as it gives intense purple colour on reacting with S^{2-} in presence of alkali.

$$Na_2[Fe(CN)_5NO] + Na_2S \Rightarrow Na_4[Fe(CN)_5NOS]$$
(Purple colour)

It also detect SO_3^{2-} ion by changing its colour to rose-red in presence of alkali.

$$Na_2[Fe(CN)_5NO] + Na_2S \rightarrow Na_4[Fe(CN)_5NOS] + H_2O$$
(rose-red)

(+III state)

Another important oxidation state of Fe is +III. The colour of Fe(III) solution is yellow-brown due to the presence of colloidal iron-oxide or FeO.OH.

Oxides and hydrated oxides :-

Hydrolysis of $FeCl_3$ forms reddish-brown ppt. of hydrous oxide, $Fe_2O_3\cdot(H_2O)_n$ rather

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forming $Fe(OH)_3$. Heating hydrous oxide ~~gives~~ at 200°C gives red-brown Fe_2O_3.

Fe_3O_4 is a mixed oxide $Fe^{II}Fe^{III}_2O_4$ which has an inverse spinel structure.

Fe_2O_3 and Fe_3O_4 are tend to be non-stoichiometric like FeO.

The freshly prepared hydrous oxide dissolves in acid giving a pale-violet colour solution of $[Fe(H_2O)_6]^{3+}$ ion. In conc. NaOH solution it forms $[Fe(OH)_6]^{3-}$ ion. Due ~~sofa~~ to solubility in both acid and base, it is amphoteric in nature, But more basic ~~than~~ in nature.

The halides are formed by directly reacting with halogens. FeI_3 does not exist as Fe^{3+} oxidises I^-. In case of aq. soln. of FeF_3, it does not give positive result for neither Fe^{3+} nor F^- as it is present as a complex anion, $[FeF_6]^{3-}$. ~~Due to the Laporte and spin forbidden transiti~~ As the transtions are Laporte forbidden and spin forbidden they, it has no ~~intense~~ colour, whereas $FeCl_3$ is almost black and $FeBr_3$ is reddish-brown due to charge-transfer. The hydrated $FeCl_3 \cdot 6H_2O$ is used as oxidising agent and it is yellow-brown in colour.

The hydrated $FeCl_3 \cdot 6H_2O$ exists as $[Fe(H_2O)_4Cl_2]Cl \cdot 2H_2O$ but HCl it exists as $[FeCl_4]^-$.

Complexes :- Fe^{3+} prefer to form complexes
08 with the ligands having oxygen as
donor site and opposes N.
09 It forms bonds with the chelating
ligands having N- as donor site but they are
10 less stable than the complexes with Fe(II).

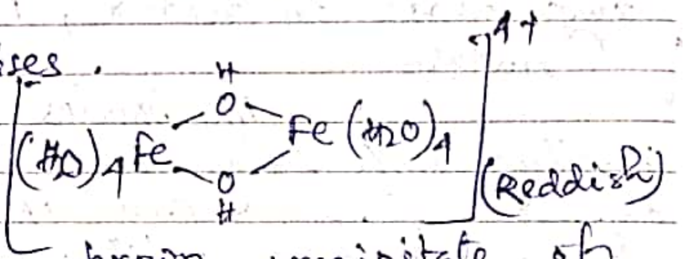
11 The aq. soln. of Fe^{3+} is acidic
in nature and tends to hydrolyse to yellow
12 solutions at pH 2-3

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H^+$$

01

at pH 4-5, it polymerises.

02 $[Fe(H_2O)_5OH]^{2+} \longrightarrow$



03

at higher pH reddish brown precipitate of
04 the hydrous oxide is formed.
The hydrated ion, $[Fe(H_2O)_6]^{3+}$ is the
05 most common ion.
It forms a colourless complex
06 with PO_4^{3-}, $[Fe(PO_4)_3]^{6-}$ and $[Fe(HPO_4)_3]^{3-}$.
for this reason,
H_3PO_4 is used as masking agent in
some estimation where it masks the colour
of Fe^{3+} whose colour interfer in the
detection of end point.

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It forms a green coloured ~~complex~~ water soluble complex with oxalate ion i.e. $[Fe(oxalate)_3]^{3-}$. Due to the ~~water~~ solubility of the complex in water, ~~It~~ ~~is~~ oxalate is used to remove stain of rust.

It forms $[Fe(SCN)(H_2O)_5]^{2+}$ along with some $Fe(SCN)_3$ and $[Fe(SCN)_4]^-$ on reacting with SCN^- ion. ~~For this reason~~ ~~so~~ The complex mixture give a blood-red coloured solution. Thus it is used ~~to~~ for the detection of Fe^{3+} qualitatively. The colour is discharged by the addition of F^- ion due to the formation of colourless $[FeF_6]^{3-}$ ion. ~~formation~~.

Another well known complex ion of Fe(III) is ~~Potassium~~ Ferricyanide or hexacyanoferrate(III). It produces deep blue coloured ~~solution~~ ~~or~~ precipitate with aq. Fe(II) and the precipitate is known as Turnbull's blue. The intense colour of the product complex, $KFe^{II}[Fe^{III}(CN)_6].xH_2O$, is due to the charge transfer ~~betw~~ between the metal centres.

It has now been established by X-ray and Mössbauer spectra that the two compounds Prussian blue and Turnbull's blue are same, $KFe^{III}[Fe^{II}(CN)_6].xH_2O$ and the colours are not different.

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Cobalt (Co)

08 General properties :- Finely divided cobalt is pyrophoric in nature like
09 iron but the compact metal is not attacked by air or water at r.t.

10 It burns in air above 300°c and forms Co_3O_4 and CoO.

11 Cobalt dissolves less readily than iron in mineral acids. The metal is not attacked by
12 aq. alkali but reacts with fused KOH at 550°c.

The metal reacts with halogens on
01 heating.

It has two important oxidation states
02 (II) and (III). In acidic medium Co(II) is more stable than Co(III).

03 Co(III) is oxidising in nature.

04

+III oxidation state

05 This oxidation state is present in some simple compounds.

06

The oxide of Co(III) can't be obtained in pure form, it only found as hydrated species, $Co_2O_3(aq)$ which can be dried upto $Co_2O_3 \cdot H_2O$.

The Co_3O_4 is a compound having both the oxidation states. It ~~also~~ has a normal spinel structure like iron, $Co^{II}Co_2^{III}O_4$. Co^{II} is in high-spin and Co^{III} is in low spin state.

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Co_2O_3 dissolves in dil. HCl :

$$Co_2O_3 + 6HCl \rightarrow 2CoCl_2 + Cl_2\uparrow + 2H_2O$$

Co_3O_4 also ~~forms~~ evolve Cl_2 with HCl soln.,

$$Co_3O_4 + 8HCl \rightarrow 3CoCl_2 + Cl_2\uparrow + 4H_2O$$

when Co_3O_4 is heated ~~to~~ above 900°C, it looses its oxygen and forms CoO.

Among halides only fluoride and chloride are known due to ~~to~~ strong oxidising power Co(III). CoF_3 is a strong fluorinating agent, and fluorinates hydrocarbons directly to fluorocarbons:

$$4CoF_3 + >CH_2 \rightarrow >CF_2 + 4CoF_2 + 2HF$$

Complex formation :- The complexes are formed with strong field ligand as in low spin complexes the electronic configuration is $t_{2g}^6 e_g^0$ which has very high CFSE value and they all are diamagnetic except CoF_6^{3-} which is paramagnetic with electronic configuration $t_{2g}^4 e_g^2$.

Co^{3+} forms most complexes ~~with~~ through N-donar sites of the ligands. Common complexes are with NH_3, ~~and~~ en, EDTA, amines, nitrite ion.

Co^{3+} complexes do not undergo substitution reaction easily. The octahedral cyanide complex is extremely and considered as non-toxic due to non-replacable CN^- ions.

The complexes ~~with~~ through oxygen donor site are also known but they are less stable. Some examples of such complexes are

$[Co(Ox)_3]^{3-}$, $[Co(acac)_3]$, where $[Co(acac)_3]$ is insoluble in water but soluble in organic solvents.

Sodium cobaltinitrite is an important complex of Co(III) which is used in both qualitative and quantitative analysis of K^+ ion.

$$Na_3[Co(NO_2)_6] + K^+ \longrightarrow \underset{\text{Yellow sparingly soluble salt,}}{K[Co(NO_2)_6]}\downarrow + Na^+$$

This sparingly soluble salt precipitates at the bottom which indicates the presence of K^+ ion in sample.

Co(III) has an biological importance. Vit. B_{12} is an important complex of Co(III). Here Co(III) is present at the centre of corrin ring system. Vit. B_{12} is used in the treatment of pernicious anaemia.

(+II) oxidation state

It is the most important oxidation state for simple compounds. With ligands stronger than water in the spectrochemical series, Co(III) becomes the preferred state due to the larger CFSE but Co(II) forms complex with weak-field ligands.

It forms some simple salts with common acids and form $CoCl_2$, $CoSO_4$, $Co(NO_3)_2$.

Its oxide, CoO is formed when steam is passed over red-hot cobalt or salts of cobalt. CoO is olive-green solid which is stable upto 1000°C and when heated in air it forms Co_3O_4. It is slightly amphoteric but more basic and reacts with acids, give various salts. It dissolves in conc. alkali and form a blue solution containing $[Co(OH)_4]^{2-}$ ion. If CoO is melted with SiO_2 and K_2CO_3 a deep blue glass, potassium cobalt(II) silicate, is formed. This 'cobalt blue glass' is used in laboratory to observe the flame colour in presence of sodium in flame test. The blue glass absorbs the intense yellow colour of sodium and we observe the flame colours of other metal ions.

On addition of NaOH in solution of Co^{2+}, it forms a blue ppt. of $Co(OH)_2$ at first then it passes to the more stable pink forms, [$\beta-Co(OH)_2$] on standing or warming the suspension.

Among the halides, the chloride is used to detect water as the hydrated chlore, $CoCl_2.6H_2O$ is pink but anhydrous $CoCl_2$ is blue.

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$$[Co(H_2O)_6]^{2+} \underset{hydrate}{\overset{heat}{\rightleftharpoons}} [Co(H_2O)_4]^{2+} + 2H_2O$$

pink blue

The hexa-aqua ion on reacting with excess Cl^- forms ~~[illegible]~~ blue $[CoCl_4]^{2-}$ ion.

$$[Co(H_2O)_6]^{2+} + 4Cl^- \longrightarrow [CoCl_4]^{2-} + 6H_2O$$

pink. blue

By ~~the~~ ~~on~~ ~~on~~ heating the hydrated salts, anhydrous salt can't be obtained as strong heating causes decomposition. Thus on heating, hydrated salts are converted into partly hydrated. Anhydrous salts are formed by direct reaction.

Complexes :-

Both the octahedral and tetrahedral complexes are common for Co^{2+}. Octahedral complexes are pink and tetrahedral complexes are blue in colour. The anhydrous $CoCl_2$ is co-ordinated tetrahedrally thus blue in colour.

Due to ~~[illegible]~~ have no centre of symmetry tetrahedral complexes easily overcome the Laporte selection rule and shows intense colours.

The calculated spin only magnetic moment of both octahedral and tetrahedral complexes are smaller than the actual magnetic moments.

In case of octahedral complexes, the electronic
08 arrangment is $t_{2g}^{6} e_g^{2}$ which ~~have~~ has orbital
contribution and in case of ~~[illegible]~~ tetrahe-
09 -dral complexes electronic distribution is $e^{4} t_{2g}^{3}$, here
spin-orbit coupling takes place. For these reasons
10 the predicted spin-only magnetic moment is
always smaller than the actual magnetic moment.
11 Co^{2+}-complexes are less stable than Co^{3+} complexes
Since there is only a small difference ~~between~~ in the
12 stability of ~~the~~ ~~two~~ the complexes of the two oxidation
states thus they exist in equilibrium. ~~The large~~
01 ~~mon~~ The large monodentate ligands
form tetrahedral complexes. Co(II) forms larger
02 number of tetrahedral complexes than any
other transition metals. Most Co(II) complexes
03 are high spin but CN^- forms low spin complexes.

04

05

Sunday 17

06

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