Chromium: Reactions

(i) Steam at red hot/heating * No reaction with water

$2Cr_{(s)} + 3H_2O_{(g)} \rightarrow Cr_2O_{3(s)} + 3H_{2(g)}$ - steam on heating.

(ii) With air : condition - heating.

$4Cr_{(s)} + 3O_{2(g)} \rightarrow 2Cr_2O_{3(s)}$

(iii) Reaction with acids

* Non oxidising acids ie HCl and dilute H_2SO_4

- Form blue solution rapidly oxidised by air to green solution.

$Cr_{(s)} + 2H^+_{(aq)} \rightarrow Cr^{2+}_{(aq)} + H_{2(g)}$ — blue

$4Cr^{2+}_{(aq)} + 4H^+_{(aq)} + O_{2(g)} \rightarrow 4Cr^{2+}_{(aq)} + 2H_2O_{(l)}$. — green solution

* oxidising acid:

- Conc H_2SO_4: $2Cr_{(s)} + 6H_2SO_{4(l)} \rightarrow Cr_2(SO_4)_{3(s)} + 6H_2O_{(l)} + 3SO_{2(g)}$

$2Cr_{(s)} + 3SO_4^{2-}{}_{(aq)} + 12H^+_{(aq)} \rightarrow 2Cr^{2+}_{(aq)} + 6H_2O_{(l)} + 3SO_{2(g)}$.

* Nitric acid 4 renders chromium passive → due to formation of thick insoluble oxide layer.

(iii) Non-metals

$2Cr_{(s)} + 3S \rightarrow Cr_2S_{3(s)}$

$2Cr_{(s)} + N_{2(g)} \rightarrow 2CrN$

$4Cr_{(s)} + 3O_{2(g)} \rightarrow 2Cr_2O_{3(s)}$.

$2Cr_{(s)} + 3Cl_{2(g)} \rightarrow 2CrCl_{3(s)}$.

(iv) With alkali

$2Cr_{(s)} + 2\bar{O}H_{(aq)} + 6H_2O_{(l)} \rightarrow 2Cr(OH)_4^-{}_{(aq)} + 3H_{2(g)}$

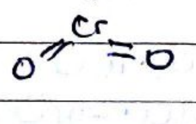
$2Cr_{(s)} + 2\bar{O}H_{(aq)} + 2H_2O_{(l)} \rightarrow 2CrO_2^-{}_{(aq)} + 3H_{2(g)}$.

Chromium (VI) compounds

* oxidising; Cr^{6+} is highly polarising, it exists as an oxo anion eg CrO_4^{2-} and $Cr_2O_7^{2-}$

CrO_3 - red crystalline solid

- Triangular planar : formed by reacting Conc H_2SO_4 with chromate (VI) or dichromates (VI)



e $Cr_2O_7^{2-}{}_{(aq)} + 2H_2SO_{4(aq)} \rightarrow 2HSO_4^-{}_{(aq)} + H_2O_{(l)} + 2CrO_{3(s)}$

$Cr_2O_7^{2-}{}_{(aq)} + 2H^+_{(aq)} \rightarrow 2CrO_{3(s)} + H_2O_{(l)}$

- decomposes on heating.

$4CrO_{3(s)} \rightarrow 2Cr_2O_{3(s)} + 3O_{2(g)}$ → dissolves in alkali solution forming a chromate.

* Acidic oxide dissolving in water

$CrO_{3(s)} + H_2O_{(l)} \rightarrow H_2CrO_{4(aq)}$

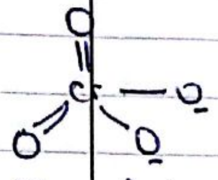
$2CrO_{3(s)} + H_2O_{(l)} \rightarrow H_2Cr_2O_{7(aq)}$.

$CrO_{3(s)} + 2NaOH_{(aq)} \rightarrow Na_2CrO_{4(aq)} + H_2O$

Chromates CrO_4^{2-} - Yellow in colour, made by oxidation of alkali chromium (III) salts with sodium peroxide.

$2Cr^{3+}_{(aq)} + 4\bar{O}H_{(aq)} + 3O_{2(aq)}^{2-} \longrightarrow 2CrO_{4(aq)}^{2-} + 2H_2O_{(l)}$.

Shape



Tetrahedral.

* only exist in neutral or alkaline solution

* In acidic solution, they turn into a dichromate, orange in colour

∴ they are 'basic'

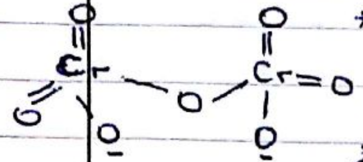
$2CrO_{4(aq)}^{2-} + 2H^+_{(aq)} \longrightarrow Cr_2O_{7(aq)}^{2-} + H_2O_{(l)}$

yellow. orange

* They are oxidising agents

$CrO_{4(aq)}^{2-} + 8H^+_{(aq)} + 3\bar{e} \longrightarrow Cr^{3+}_{(aq)} + 4H_2O_{(l)}$

Dichromates $Cr_2O_7^{2-}$ - orange in colour.



* made by acidifying chromates (VI).

$2CrO_{4(aq)}^{2-} + 2H^+_{(aq)} \longrightarrow Cr_2O_{7(aq)}^{2-} + H_2O_{(l)}$.

hexavalent amphoteric

$Cr_2O_{7(aq)}^{2-} + 2\bar{O}H_{(aq)} \longrightarrow 2CrO_{4(aq)}^{2-} + H_2O_{(l)}$.

yellow

orange $Cr_2O_{7(aq)}^{2-} + 2H^+_{(aq)} \longrightarrow 2CrO_{3(s)} + H_2O_{(l)}$.

(red)

conc. H_2SO_4.

oxidising agents:

$Cr_2O_{7(aq)}^{2-} + 14H^+_{(aq)} + 6\bar{e} \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$.

(i) $H_2S_{(aq)} \longrightarrow 2H^+_{(aq)} + S_{(s)} + 2\bar{e}$ $\quad 2I^-_{(aq)} \longrightarrow I_{2(aq)} + 2\bar{e}$

$SO_{3(aq)}^{2-} + H_2O_{(l)} \longrightarrow SO_{4(aq)}^{2-} + 2H^+_{(aq)} + 2\bar{e}$ $\quad Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + \bar{e}$

$S^{2-}_{(aq)} \longrightarrow S_{(s)} + 2\bar{e}$ } readily oxidised.

Primary standard • high molecular mass;
• stable on storage; • not strong oxidising agent & can be acidified by HCl.

Chromium III compounds (+3) → most stable

- Green due to existence of $Cr(H_2O)_6^{3+}$
- solution is acidic, because Cr^{3+} ions exist as $Cr(H_2O)_6^{3+}$ ions undergoes hydrolysis forming hydroxonium ions which make the soln acidic. $Cr^{3+}_{(aq)} + 3H_2O_{(l)} \longrightarrow Cr(OH)_{3(s)} + 3H^+_{(aq)}$.

$Cr(H_2O)_{6(aq)}^{3+} + 3H_2O_{(l)} \rightleftharpoons Cr(OH)_3(H_2O)_{3(s)} + 3H_3O^+_{(aq)}$

Chromium (III) hydroxide → Green ppt

$Cr^{3+}_{(aq)} + 3\bar{O}H_{(aq)} \longrightarrow Cr(OH)_{3(s)}$ or } ppn

$2Cr^{3+}_{(aq)} + 3CO_{3(aq)}^{2-} + 3H_2O_{(l)} \longrightarrow 2Cr(OH)_{3(s)} + 3CO_{2(g)}$

Amphoteric: $Cr(OH)_{3(s)} + 3H^+_{(aq)} \longrightarrow Cr^{2+}_{(aq)} + 3H_2O_{(l)}$.

conc. alkali

$Cr(OH)_{3(s)} + \bar{O}H_{(aq)} \longrightarrow Cr(OH)^-_{4(aq)}$.

$Cr(OH)_{3(s)} + \bar{O}H_{(aq)} \longrightarrow CrO^-_{2(aq)} + 2H_2O_{(l)}$

$Cr(OH)_{3(s)} + 3\bar{O}H_{(aq)} \longrightarrow Cr(OH)^{3-}_{6(aq)}$

Green soln.

oxidised by H_2O_2 in alkaline

$2Cr(OH)_{3(s)} + 3H_2O_{2(aq)} + 4\bar{O}H_{(aq)} \longrightarrow 2CrO_{4(aq)}^{2-} + 8H_2O$

Green yellow.

Chromium (II) cpds → strong reducing agents

$Cr_{(s)} + 2HCl_{(aq)} \longrightarrow CrCl_{2(aq)} + H_{2(g)}$.

$Cr^{2+}_{(aq)} + 2CH_3CO\bar{O} \longrightarrow Cr(CH_3COO)_2$ red ppt.

$Cr^{2+}_{(aq)} + 2\bar{O}H_{(aq)} \longrightarrow Cr(OH)_{2(s)}$ yellow ppt.

Rxn must be carried out in absence of air;

$Cr^{2+} \longrightarrow Cr^{3+}_{(aq)} + \bar{e}$ $\quad +0.41V$.

Chromium III oxide Cr_2O_3 (Green solid)

* PPn: heating chromium in a stream of oxygen

$4Cr_{(s)} + 3O_{2(g)} \longrightarrow 2Cr_2O_{3(s)}$

or Heating chromium (III) hydroxide.

$2Cr(OH)_{3(s)} \longrightarrow Cr_2O_{3(s)} + 3H_2O_{(l)}$.

Amphoteric

$Cr_2O_{3(s)} + 6H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 3H_2O_{(l)}$

conc alkali

$Cr_2O_{3(s)} + 2\bar{O}H_{(aq)} \longrightarrow 2CrO^-_{2(aq)} + H_2O_{(l)}$

$Cr_2O_{3(s)} + 2\bar{O}H_{(aq)} + 3H_2O_{(l)} \rightarrow 2Cr(OH)^-_{4(aq)}$

$Cr_2O_{3(s)} + 6\bar{O}H_{(aq)} + 3H_2O_{(l)} \rightarrow 2Cr(OH)^{3-}_{6(aq)}$.

Chromium III chloride → green solid.

- Pass chlorine over heated chromium.

$2Cr_{(s)} + 3Cl_{2(g)} \longrightarrow 2CrCl_{3(s)}$.

exists as $CrCl_3 \cdot 6H_2O$; shows three isomers.

$Cr(H_2O)_6Cl_3$

$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

Chromium (III) sulphate $\cdot 6H_2O$ → shows isomer

$Cr(H_2O)_6SO_4$.

Similarity btn chemistry of chromium and lead:

① Form amphoteric oxides on heating:

$2Pb_{(s)} + O_{2(g)} \rightarrow 2PbO_{(s)}$.

$4Cr_{(s)} + 3O_{2(g)} \rightarrow 2Cr_2O_{3(s)}$

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② React with dry chlorine on heating

$Pb_{(s)} + Cl_{2(g)} \rightarrow PbCl_{2(s)}$

$Cr_{(s)} + 3Cl_{2(g)} \rightarrow 2CrCl_{3(s)}$.

③ Amphoteric oxides

$PbO_{(s)} + 2\bar{O}H_{(aq)} + H_2O_{(l)} \rightarrow Pb(OH)_4^{2-}$ } alkali

$PbO_{(s)} + 2\bar{O}H_{(aq)} \rightarrow PbO_2^{2-}{}_{(aq)} + H_2O_{(l)}$ }

$PbO_{(s)} + 2H^+_{(aq)} \rightarrow Pb^{2+}_{(aq)} + H_2O$ } Acid

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$Cr_2O_{3(s)} + 2\bar{O}H_{(aq)} \rightarrow 2CrO_2^-{}_{(aq)} + H_2O_{(l)}$ } alkali

$Cr_2O_{3(s)} + 2\bar{O}H_{(aq)} + 3H_2O_{(l)} \rightarrow 2Cr(OH)_4^-{}_{(aq)}$]

$Cr_2O_{3(s)} + 6H^+_{(aq)} \rightarrow Cr^{2+}_{(aq)} + 3H_2O_{(l)}$.

④ Both hydroxides are soluble in NaOH solution.

$Pb(OH)_{2(s)} + 2\bar{O}H_{(aq)} \rightarrow Pb(OH)_4^{2-}{}_{(aq)}$; colourless } i.e. form precipitates that dissolve in excess.

$Cr(OH)_{3(s)} + \bar{O}H_{(aq)} \rightarrow Cr(OH)_4^-{}_{(aq)}$ a green soln. }

⑤ metals don't react with cold H_2O & steam.

⑥ React with hot concentrated sulphuric acid.

$Pb_{(s)} + 2H_2SO_{4(l)} \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} + SO_{2(g)}$

$2Cr_{(s)} + 6H_2SO_{4(l)} \rightarrow Cr_2(SO_4)_{3(s)} + 6H_2O_{(l)} + 3SO_{2(g)}$.

Analysis of Chromium (III) solution.

~~- Green ppt in excess NaOH~~

Analysis of chromium (III) cation:

① Green ppt soluble in excess NaOH.

② Addition of NaOH dropwise till in excess followed by H_2O_2

$2Cr(OH)_{3(s)} + 4\bar{O}H_{(aq)} + 3H_2O_{2(l)} \rightarrow 2CrO_4^{2-}{}_{(aq)} + 8H_2O_{(l)}$

$2Cr^{3+}_{(aq)} + 10\bar{O}H_{(aq)} + 3H_2O_{2(l)} \rightarrow 2CrO_4^{2-}{}_{(aq)} + 8H_2O_{(l)}$

yellow.

④ sodium carbonate – Bubbles of colourless gas & green ppt;

2[illegible]$^{3+}_{(aq)} + 3CO_3^{2-}{}_{(aq)} + 3H_2O_{(l)} \rightarrow 2Cr(OH)_{3(s)} + 3CO_{2(g)}$.

* Formation of chromate can be confirmed by adding lead(II) ethanoate; yellow ppt formed

$Pb^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \rightarrow PbCrO_{4(s)}$.

③ Addition dilute NH_3:
Green ppt insoluble in excess.

$Cr^{3+}_{(aq)} + 3\bar{O}H_{(aq)} \rightarrow Cr(OH)_{3(s)}$

yellow ppt ↓ f

$BaCrO_{4(s)}$

red ppt ← Ag_2CrO_4

Examples:

1 (a)(i) Write the electronic configuration of chromium
(ii) state three characteristics of chromium as a transitional metal.

(b) chromium (III) chloride was dissolved in water and the solution tested with litmus. State what was observed and explain your answer. ✓

(c) Ammonia solution was added dropwise to an aqueous solution of chromium (III) salt until in excess.
(i) state what was observed ✓
(ii) Write equation for the reaction.

③ Explain the following observation

• When sodium hydroxide solution is added dropwise until in excess to potassium chromium (III) sulphate solution, a green ppt is formed, that dissolves to form a deep green solution. On addition of H_2O_2 the solution turns ✓ from green to yellowish brown.

⑤ A dark purple crystalline solid Z, dissolves in water to give a violet solution. When aqueous sodium hydroxide is added dropwise until in excess, a green ppt was formed which dissolved in excess to give a green solution.

(a) identify the cation in Z
(b) Write the formulae of the species responsible for the formation of
(i) violet solution
(ii) green solution
(c) When H_2O_2 was added to the green solution a yellow solution was formed which on treatment of ethanoate solution a yellow solid was formed.
Write the equation for the reaction leading to the formation of (i) green solution (ii) yellow solid ✓
(ii) yellow solution

② (a) chromium is a transition element. State three properties of transition elements.
(b) Write electronic configuration of chromium.
(c) Using equations to illustrate your answer, describe how chromium reacts with
(i) water
(ii) dilute hydrochloric acid ✓
(d) state what would be observed and write eqn for the reaction that takes place when NaOH is added dropwise until in excess to an aqueous solution of chromium (III) sulphate. ✓

④ State what would be observed and write equation for the reaction that would take place when; sodium sulphite is added ✓ to a solution of acidified potassium dichromate (VI)

⑥ (a) State three xtics of chromium as a transition metal. ✓
(b) A solution of potassium dichromate (VI) was added to an acidified solution of iron(II) sulphate
(i) State what was observed.
(ii) Write the ionic equation for the reaction that took place
(c)(i) Write the structural formulae of isomers of chromium (III) chloride, $CrCl_3 \cdot 6H_2O$
(ii) State one way of distinguishing the isomers.

④ Chromium (III) sulphate was dissolved in water and a few drops of concentrated sodium carbonate solution added to the solution.

(i) state what was observed

(ii) Give a reason for your answer and write eqns for this reactions.

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b) Potassium chromate was dissolved in water, state the shape of the chromate ion.

(c) To the solution in (b) was added a few drops of dilute sulphuric acid followed by aqueous sodium hydroxide dropwise until in excess.

(i) State what was observed

(ii) Write equations for the reactions that took place.

⑤ a. State the common oxidation states of chromium and lead

(b) Discuss the similarities in the chemistry of chromium and lead. (our answer should include

Question

(i) reactions leading to formation of complexes

(ii) reactions with sodium hydroxide.

Manganese $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$.

main o.s +4; +7 and +2.

Reactions

- Burns in air forming red oxide.

$3Mn_{(s)} + 2O_{2(g)} \longrightarrow Mn_3O_{4(s)}$

- react with hot water / steam on heating

$Mn_{(s)} + 2H_2O_{(g)} \longrightarrow Mn(OH)_{2(s)} + H_{2(g)}$

- With acids

(a) dilute acids

$Mn_{(s)} + 2H^+_{(aq)} \longrightarrow Mn^{2+}_{(aq)} + H_{2(g)}$

* dilute HCl, HNO$_3$.
H$_2$SO$_4$

(b) concentrated acids

* conc H$_2$SO$_4$

$Mn_{(s)} + 2H_2SO_{4(l)} \longrightarrow MnSO_4 + SO_{2(g)} + 2H_2O_{(l)}$

* conc ~~H$_2$SO$_4$~~, HNO$_3$

$Mn_{(s)} + 4HNO_{3(l)} \longrightarrow Mn(NO_3)_2 + 2NO_2 + 2H_2O_{(l)}$.

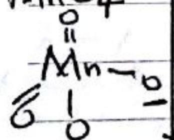
(c) With nonmetals (N_2; C; Cl_2; S)

- react on heating

$3Mn_{(s)} + N_{2(g)} \longrightarrow Mn_3N_{2(s)}$.

Manganese (VI) compounds

MnO_4^{2-} - green solid - $\frac{K}{Na}$?



- The ion disproportionates in presence of an acid or H_2O

$3MnO^{2-}_{4(aq)} + 4H^+_{(aq)} \longrightarrow 2MnO_4^- + MnO_{2(s)} + 2H_2O_{(l)}$.

$3MnO^{2-}_{4(aq)} + 2H_2O_{(l)} \longrightarrow 2MnO^-_{4(aq)} + MnO_{2(s)} + 4\bar{O}H$

4

Green solution turns to purple and a black / brown solid.

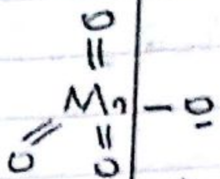
Oxidising property

$MnO^{2-}_{4(aq)} + 2H_2O_{(l)} + 2\bar{e} \longrightarrow MnO_{2(s)} + 4\bar{O}H_{(aq)}$.

MnO_4^{2-} only stable in alkaline solution, because disproportionates in neutral or acidic soln; even bubbling CO_2 through the solution causes disproportionation

$CO_{2(g)} + H_2O_{(l)} \longrightarrow H_2CO_3 \rightleftharpoons H^+ + HCO_3^{2-}$.

Compounds of Mn MnO_4^-



tetrahedral

+7 o.s

Manganate (VII) ie $KMnO_4$.

- powerful oxidising agent.

$2Mn^{2+}_{(aq)} + 5BiO^-_{3(aq)} + 14H^+_{(aq)} \longrightarrow 2MnO^-_{4(aq)} + 5Bi^{3+}_{(aq)} + 7H_2O_{(l)}$

* formed when Mn^{2+} is oxidised by strong oxidising agents.

* oxidising properties.

In acidic media

$MnO^-_{4(aq)} + 8H^+_{(aq)} + 5\bar{e} \longrightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$

$C_2O_4^{2-} \longrightarrow 2CO_{2(g)} + 2\bar{e}$

$H_2O_{2(l)} \longrightarrow O_{2(g)} + 2H^+_{(aq)} + 2\bar{e}$

$Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + \bar{e}$

$NO^-_{2(aq)} + H_2O_{(l)} \longrightarrow NO^-_{3(aq)} + 2H^+_{(aq)} + 2\bar{e}$

$SO^{2-}_{3(aq)} + H_2O_{(l)} \longrightarrow SO^{2-}_{4(aq)} + 2H^+_{(aq)} + 2\bar{e}$

$2I^-_{(aq)} \longrightarrow I_{2(aq)} + 2\bar{e}$

$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2\bar{e}$

In neutral or slightly alkaline soln

$MnO^-_{4(aq)} + 2H_2O_{(l)} + 3\bar{e} \longrightarrow MnO_{2(s)} + 4\bar{O}H_{(aq)}$

* weaker oxidising agent under these conditions.

- oxidises iodide to iodate not iodine.

$2MnO^-_{4(aq)} + H_2O_{(l)} + I^-_{(aq)} \longrightarrow 2MnO_{2(s)} + 2\bar{O}H_{(aq)} + IO^-_{3(aq)}$

Uses $KMnO_4$

- Volumetric analysis
- quantitative analysis of oxalates, SO_3^{2-}; Cl^-
- oxidising agent in organic synthesis.

Not a 1° standard

* cannot be obtained in a high degree of purity free from MnO_2

* deposits MnO_2 on standing so unstable

$4MnO^-_{4(aq)} + 4H^+_{(aq)} \longrightarrow 4MnO_{2(s)} + 3O_{2(g)} + 2H_2O_{(l)}$

* cannot be acidified by conc. HCl.

$2MnO^-_{4(aq)} + 10Cl^-_{(aq)} + 16H^+_{(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + 5Cl_{2(g)} + 8H_2O_{(l)}$

Adv in volumetric analysis

- No indicator required
- oxidises a wide range of soln
- Fairly stable in H_2O
- High relative molecular mass -

Manganese (IV) compounds – MnO_2

- Formed by heating $Mn(NO_3)_2 \rightarrow MnO_{2(s)} + 2NO_{2(g)}$.

Strong oxidizing agent

$MnO_{2(s)} + 4H^+_{(aq)} + 2e^- \rightarrow Mn^{2+}_{(aq)} + 2H_2O_{(l)}$

① amphoteric

(a) with acids:

$2MnO_2 + 2H_2SO_{4(l)} \rightarrow 2MnSO_{4(aq)} + 2H_2O_{(l)} + O_{2(g)}$.

$2MnO_{2(s)} + 4H^+_{(aq)} \rightarrow 2Mn^{2+}_{(aq)} + 2H_2O_{(l)} + O_{2(g)}$

conc H_2SO_4 on heating.

- cold conc HCl;

$MnO_2 + 4H^+_{(aq)} + 6Cl^-_{(aq)} \rightarrow [MnCl_6]^{2-}_{(aq)} + 2H_2O_{(l)}$

Warm conc HCl

$MnO_{2(s)} + 4HCl_{(l)} \rightarrow MnCl_{2(aq)} + 2H_2O_{(l)} + Cl_{2(g)}$

Mn (II) cpds

MnO – basic oxide:

$MnO_{(s)} + 2H^+_{(aq)} \rightarrow Mn^{2+}_{(aq)} + H_2O_{(l)}$

$Mn(OH)_2$ ⇒ White ppt; Add NaOH to Mn^{2+}

$Mn^{2+}_{(aq)} + 2OH^- \rightarrow Mn(OH)_2$ & turns brown due to oxidation to brown solid

$2Mn(OH)_{2(s)} + O_{2(g)} \rightarrow 2MnO_2 \cdot H_2O$

$2Mn(OH)_2 + \frac{1}{2}O_{2(g)} \rightarrow Mn_2O_3 \cdot 2H_2O_{(l)}$

$Mn(NO_3)_{2(s)} \rightarrow MnO_{2(s)} + 2NO_{2(g)}$

decomposes on heating

Analysis of Mn^{2+} , insoluble in excess

* NaOH ⇒ White ppt turning brown on standing
* NH_3 ⇒ similar observations ↑.
* Add conc HNO_3; followed by solid $NaBiO_3$ or PbO_2 and heat ⇒ Purple soln formed.

Examples of complexes of Mn

* $Mn(H_2O)_6^{2-}$; $Mn(CN)_6^{4-}$; $Mn(CN)_6^{3-}$

Examples

① Write equation and state what would be observed when manganate (VI) is hydrolysed by H_2O ✓

② Determine the oxidation states of manganese in $MnO_4^-{}_{(aq)}$, MnO_4^{2-} and MnO_2 ✓

(ii) State what would be observed if carbon dioxide was bubbled through a solution containing manganate (VI) ions ✓

③ a Write

(i) the electronic configuration of manganese atom ✓

(ii) possible oxidation states of manganese

(b)(i) Write the half equation for the reduction of potassium permanganate in acidic medium.

(ii) State the oxidation change in the oxidation states of manganese in b(i) above.

(c) State three advantages of using potassium permanganate in volumetric analysis

(d) Briefly explain why hydrochloric acid and nitric acid are not used for acidifying potassium [illegible] in volumetric analysis.

(b) with caustic alkali

$MnO_{2(s)} + 2OH^-_{(aq)} \rightarrow MnO_3^{2-}{}_{(aq)} + H_2O_{(l)}$.

② decomposes on heating

$3MnO_{2(s)} \rightarrow Mn_3O_{4(s)} + O_{2(g)}$

→ oxidising properties

* Hot oxalates in presence of dilute Conc H_2SO_4

$C_2O_4^{2-}{}_{(aq)} \rightarrow 2CO_{2(g)} + 2e^-$

* conc HCl to chlorine on heating

$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$

Manganese (II)

- most stable because of the presence of presence of five singly occupied 3d-orbital in the manganese (II) ion.
- strong oxidising agents like lead(IV) oxide and sodium bismuthate in acidic condition oxidise Mn^{2+} to MnO_4^- ion (purple).

$2Mn^{2+}_{(aq)} + 5BiO_3^-{}_{(s)} + 14H^+_{(aq)} \rightarrow 2MnO_4^-{}_{(aq)} + 5Bi^{2+}_{(aq)} + 7H_2O_{(l)}$

$2Mn^{2+}_{(aq)} + 5PbO_{2(s)} + 4H^+_{(aq)} \rightarrow 2MnO_4^-{}_{(aq)} + 5Pb^{2+}_{(aq)} + 2H_2O_{(l)}$

MnS pptd by adding H_2S to a soln of Mn (II) salts in presence of ammonia and ammonium chloride the the solubility prod of the sulphide is too high for it to pptate in acidic solution.

$Mn^{2+}_{(aq)} + S^{2-}_{(aq)} \rightarrow MnS_{(s)}$.

dissolves in dilute mineral acids

$MnS_{(s)} + 2HCl_{(aq)} \rightarrow MnCl_{2(aq)} + H_2S_{(g)}$

* Addition H_2O_2 soln
- alkaline medium, followed by H_2O_2; dark brown / Black precipitate formed.

$Mn^{2+}_{(aq)} + H_2O_{2(aq)} + 2OH^-_{(aq)} \rightarrow MnO_{2(s)} + 2H_2O_{(l)}$

* Addition of Na_2CO_3 ⇒ White ppt formed: $MnCO_3$;

MnF_6^{2-}; MnO_4^{2-}; MnO_4^-

(e) Explain what would be observed if aqueous sodium hydroxide solution was added to a solution containing manganese (II) ions drop wise until in excess ✓

*(f) Name a reagent apart from aqueous ammonia ✓ and sodium hydroxide solution that can be used to distinguish manganese (II) ions from nickel (II) ions. state what would be observed if each of them is separately treated with the reagent you have named.

④ (i) Write the outer configuration of manganese

(ii) State the possible oxidation states of manganese

(iii) How does the acidity of the oxides of manganese vary with increasing oxidation states.

(iv) What is the change in oxidation state of manganese when potassium manganate (VII) is reduced under alkaline conditions

(b) state four applications of potassium permanganate (VII) in the laboratory as an oxidising agent.

5 (a) Iron (II) sulphate is normally used to standardise a solution of potassium manganate (VII) acidified using sulphuric acid.

(i) Write equation for the reaction between $KMnO_4$ and iron (II) sulphate.

Do not write in this margin

Write on both sides of the paper

(ii) State why hydrochloric acid is not used to acidify potassium manganate (VII) solution ✓

(b) 20cm³ of acidified solution of potassium manganate 0.02M reacted exactly with 25cm³ of sodium nitrite. Calculate the concentration of sodium nitrite in moles per litre.

6 Potassium manganate (VII) is not used as a 1° standard in volumetric analysis and has to be standardised.

(i) What is meant by the term primary standard.

(ii) State three xtics of 1° standard.

Question

(iii) Explain why potassium manganate (VII) is not used as a primary standard.

(iv) Name one substance other than oxalic acid that can be used as a primary standard for potassium manganate (VII).

(b) Explain why hydrochloric acid is not usually used to acidify solutions of potassium manganate (VII).

(c) Acidified $KMnO_4$ reacts with ethanedioic acid

(i) Write the half equations for the reaction

(ii) the overall equation for the reaction.

(d) 20.0cm³ of a 0.01M manganate (VII) ion solution required exactly 16.65cm³ of solution containing 1.8gl⁻¹ of oxalate $(COO^-X^+)_2 \cdot 2H_2O$ calculate atomic mass of X.

Iron $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$.

common o's +2; +3 : Fe^{2+}; Fe^{3+}

ores

* iron pyrites FeS_2 Magnetite Fe_3O_4

* Haematite Fe_2O_3 ✓ Limonite $Fe_2O_3 \cdot H_2O$ spathic iron $FeCO_3$.

Extraction

* Blast furnace.

* Iron ore + limestone + coke are fed into the furnace

* Hot air is passed thro' the furnace from bottom

* coke burns $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

* coke reduces CO_2 to CO;

$CO_{2(g)} + C_{(s)} \longrightarrow 2CO_{(g)}$.

* CO at 700°C reduces iron oxide

$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(l)} + 3CO_{2(g)}$

* Lime stone decomposes at 800°C

$CaCO_3 \longrightarrow CaO_{(s)} + CO_{2(g)}$; CaO combines with impurities forming slag; calcium silicate.

$CaO_{(s)} + SiO_2 \longrightarrow CaSiO_{3(l)}$

$CaO_{(s)} + Al_2O_3 \longrightarrow CaAl_2O_{4(l)}$.

* Molten iron sinks at the bottom while slag floats on top; tapped off separately.

* Molten iron = pig or cast iron = impure (P, C, S, Si)

* Purified and converted to steel.

Chemical properties

① air

* In presence of moisture, iron readily rusts forming a brown solid.

$2Fe_{(s)} + \frac{3}{2}O_2 + xH_2O \longrightarrow Fe_2O_3 \cdot xH_2O$

* Not affected by dry air at room temperature.

* Heated iron reacts with oxygen to form black solid Fe_3O_4 and iron (III) oxide.

$3Fe_{(s)} + 2O_{2(g)} \longrightarrow Fe_3O_{4(s)}$

$4Fe_{(s)} + 3O_{2(g)} \longrightarrow 2Fe_2O_{3(s)}$.

② With H_2O

* Pure iron doesn't react with pure cold water.

* Heated iron at red hot reacts with water forming $H_{2(g)}$

$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$.

③ With acids.

Non oxidising acids dilute HCl & dilute H_2SO_4.

$Fe_{(s)} + 2H^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + H_{2(g)}$ because it is fairly electropositive. iron II salt is obtained.

Oxidising acids

Dilute HNO_3 ⇒ Iron (III) salt is formed.

Conc HNO_3 ⇒ renders the metal passive due to the formation of Fe_3O_4 on the metal.

conc H_2SO_4 and heat ⇒ Iron (III) salt formed + SO_2

$2Fe_{(s)} + 6H_2SO_{4(l)} \longrightarrow Fe_2(SO_4)_{3(aq)} + 6H_2O_{(l)} + 3SO_{2(g)}$.

④ With non metals.

React with non metals on heating

$Fe_{(s)} + S_{(s)} \longrightarrow FeS$ (black solid)

$2Fe_{(s)} + 3Cl_{2(g)} \longrightarrow 2FeCl_{3(s)}$ (black sublimate).

Compounds

+3 O.S more stable because has half filled 3d orbital than +2 O.S.

O.S +2 compounds

① FeO ⇒ black solid.

formation

$FeC_2O_{4(s)} \longrightarrow FeO_{(s)} + CO_{(g)} + CO_{2(g)}$

* Readily oxidised when heated in air

$4FeO_{(s)} + O_{2(g)} \longrightarrow 2Fe_2O_{3(s)}$

* Basic oxide readily reacting with dilute acid

$FeO_{(s)} + 2H^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + H_2O_{(l)}$.

* Disproportionates when heated in an inert atmosphere into iron and Fe_3O_4.

$4FeO_{(s)} \longrightarrow Fe_{(s)} + Fe_3O_{4(s)}$

② Iron (II) hydroxide

\- Green ppt formed when aqueous NaOH or NH_3 is added to a solution of iron (II) salt.

$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Fe(OH)_{2(s)}$

rapidly oxidised to brown iron (III) hydroxide when exposed to air

$4Fe(OH)_2 + O_{2(g)} + 2H_2O_{(l)} \longrightarrow 4Fe(OH)_{3(s)}$.

* Readily dissolves in dilute acids forming a green solution.

$Fe(OH)_2 + H^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + H_2O_{(l)}$

$Fe^{2+}_{(aq)} + 6H_2O_{(l)} \rightleftharpoons Fe(H_2O)_6^{2+}$.

③ Iron(II) carbonate.
→ White precipitate
$Fe^{2+}_{(aq)} + CO_3^{2-} \rightarrow FeCO_3$.
* must be formed from boiled water which doesn't contain air because it oxidises readily to $Fe(OH)_3$.
* Iron(III) carbonate doesn't exist because iron(III) ions are more acidic than iron(II) ions.
$Fe(H_2O)_6^{3+}{}_{(aq)} + 3CO_3^{2-}{}_{(aq)} \rightleftharpoons Fe(H_2O)_3(OH)_{3(s)} + 3HCO_3^-{}_{(aq)}$
or
$Fe(OH_2)_6^{3+} + 3CO_3^{2-}{}_{(aq)} \rightleftharpoons Fe(H_2O)_3(OH)_{3(s)} + 3H_2O_{(l)} + 3CO_{2(g)}$
On heating
$2Fe(H_2O)_3(OH)_3 \rightarrow Fe_2O_{3(s)} + 9H_2O_{(l)}$
④ Iron(II) sulphide ⇒ black solid.
$FeS_{(s)} + 2H^+_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H_2S_{(g)}$.
⑤ Iron(II) sulphate ⇒ efflorescent solid
$Fe + H_2SO_4 \rightarrow FeSO_4 + H_{2(g)}$; crystallisation $FeSO_4 \cdot 7H_2O$
* $FeSO_4 \cdot 7H_2O \xrightarrow{\text{heating}} FeSO_{4(s)} + 7H_2O_{(l)}$
green crystals white/dirty yellow.
* strong heating
$2FeSO_{4(s)} \rightarrow Fe_2O_{3(s)} + SO_{2(g)} + SO_{3(g)}$.
* oxidised by nitric acid (conc)
$6FeSO_{4(aq)} + 3H_2SO_{4(aq)} + 2HNO_{3(aq)} \rightarrow 3Fe_2(SO_4)_{3(aq)} + 4H_2O_{(l)} + 2NO_{(g)}$
⑥ Iron(II) ammonium sulphate $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$
* Not efflorescent * stable in air as does not get oxidised
* used as a primary standard in standardising $KMnO_4$ solutions
⑦ Iron(II) halides.
* $Fe_{(s)} + 2HCl_{(g)} \xrightarrow{\text{heating}} FeCl_2$ (anhydrous – white solid) $+ H_{2(g)}$
* $Fe + 2HCl_{(aq)} + 4H_2O \rightarrow FeCl_2 \cdot 4H_2O_{(s)} + H_{2(g)}$
pale green solid.
* Action of Cl_2 or F_2 directly on metal yields iron(III) salts.

Aqueous chemistry of iron(II) ions

① NaOH(aq) and $NH_{3(aq)}$.
→ Green ppt insoluble in excess, turns brown on standing.
$Fe^{2+}_{(aq)} + 2OH^- \rightarrow Fe(OH)_{2(s)}$ pale green
$4Fe(OH)_{2(s)} + O_{2(g)} + 2H_2O \rightarrow 4Fe(OH)_{3(s)}$ (brown).
② Potassium hexacyanoferrate(II) solution
→ White ppt which turns rapidly blue.
③ Potassium hexacyanoferrate(III) solution
→ Dark blue ppt formed.
$Fe^{2+}_{(aq)} + Fe(CN)_6^{3-}{}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Fe(CN)_6^{4-}{}_{(aq)}$
$Fe^{3+}_{(aq)} + Fe(CN)_6^{4-} + K^+ \rightarrow KFe(Fe(CN)_6)$
Blue ppt
④ Potassium thiocyanate
→ No observation but gives some coloration after due to aerial oxidation of $Fe^{2+} \rightarrow Fe^{3+}$.
⑤ Dimethylglyoxime solution (DMG)
→ shows red solution.

Iron(III) compounds

* solutions in water strongly acidic because iron(III) ions exist as $Fe(OH_2)_6^{3+}$ in solution. Fe^{3+} has a small cationic radius, high charge & high polarising power, undergoes hydrolysis in water forming hydroxonium ions in solution making the solution acidic.
$Fe(H_2O)_6^{3+} + 3H_2O_{(l)} \rightleftharpoons Fe(OH)_3(H_2O)_{3(s)} + 3H_3O^+_{(aq)}$
∴ These cations react with
(a) $Mg + 2H_3O^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_2O_{(l)} + H_{2(g)}$
or $Mg_{(s)} + 2H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_{2(g)}$
→ liberating hydrogen gas.

* React with sodium hydrogen carbonate solution forming brown ppt and bubbles of a colourless gas.
$2Fe^{3+}_{(aq)} + 3CO_3^{2-}{}_{(aq)} + 3H_2O_{(l)} \rightarrow 2Fe(OH)_{3(s)} + 3CO_{2(g)}$
$2Fe(H_2O)_6^{3+}{}_{(aq)} + 3CO_3^{2-}{}_{(aq)} \rightarrow 2Fe(OH)_3(H_2O)_{3(s)} + 3CO_{2(g)} + 3H_2O_{(l)}$

Iron(III) oxide Fe_2O_3

$2Fe(OH)_{3(s)} \rightarrow Fe_2O_{3(s)} + 3H_2O_{(l)}$
$2FeSO_{4(s)} \rightarrow Fe_2O_{3(s)} + SO_{2(g)} + SO_{3(g)}$
Amphoteric:
$Fe_2O_{3(s)} + 6H^+_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 3H_2O_{(l)}$
$Fe_2O_{3(s)} + 2OH^-_{(aq)} \rightarrow 2FeO_2^- + H_2O_{(l)}$
$Fe_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 2Fe(OH)_4^-{}_{(aq)}$.
$Fe_2O_{3(s)} + 6OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 2Fe(OH)_6^{3-}$
Reactions similar to those of Al_2O_3

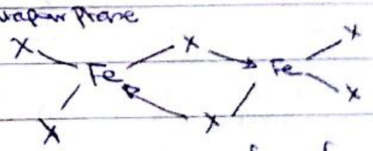
Fe_3O_4

$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$
* React with acid to form a mixture of iron(II) & iron(III) salts
$Fe_3O_{4(s)} + 8H^+_{(aq)} \rightarrow Fe^{2+}_{(aq)} + Fe^{3+}_{(aq)} + 4H_2O_{(l)}$

Iron(III) hydroxide

$Fe^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Fe(OH)_{3(s)}$ Brown ppt.
Amphoteric
$Fe(OH)_{3(s)} + 3H^+_{(aq)} \rightarrow Fe^{3+}_{(aq)} + 3H_2O_{(l)}$.
$Fe(OH)_{3(s)} + OH^-_{(aq)} \rightarrow Fe(OH)_4^-$ or
$Fe(OH)_{3(s)} + OH^-_{(aq)} \rightarrow FeO_2^-{}_{(aq)} + H_2O_{(l)}$.
Heating ⇒ $Fe(OH)_3 \rightarrow Fe_2O_{3(s)} + 3H_2O_{(l)}$.

Iron(III) halides ⇒ $2Fe_{(s)} + 3X_{2(g)} \xrightarrow{\text{heating}} 2FeX_{3(s)}$
$FeCl_3$ & $FeBr_3$ ⇒ covalent solids that dimerise in vapour phase



at high temperature decomposes to iron(II) halide
$2FeX_{3(s)} \rightarrow 2FeX_{2(s)} + X_{2(g)}$
* Salts are readily hydrolysed in solution. eg
$FeCl_{3(s)} + 3H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 3HCl_{(aq)}$.
* Iron(III) iodide cannot be obtained in pure state because solution containing iron(III) ions readily oxidise iodide ions to iodine.
$2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + I_{2(aq)}$. I_2 is not a very powerful oxidising agent to convert Fe^{2+} to Fe^{3+}.

$Fe_2(SO_4)_3$

$2FeSO_{4(aq)} + H_2SO_{4(aq)} + H_2O_{2(aq)} \rightarrow Fe_2(SO_4)_{3(aq)} + 2H_2O_{(l)}$
When heated
$Fe_2(SO_4)_{3(s)} \rightarrow Fe_2O_{3(s)} + 3SO_{3(g)}$

Aqueous chemistry of iron(III) ions

① NaOH and aqueous NH_3 ⇒ brown ppt insoluble in excess
$Fe^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Fe(OH)_{3(s)}$.
② Potassium hexacyanoferrate(II) solution
* Dark blue ppt
③ (III) solution ⇒ Brown coloration
④ Potassium thiocyanate solution ⇒ Blood red solution.

Inter conversion btn Fe^{2+} and Fe^{3+}

$Fe^{2+} \longrightarrow Fe^{3+}_{(aq)} + \bar{e}$

(a) Conc HNO_3 ⇒ Brown fumes NO_2 evolved

$6Fe^{2+}_{(aq)} + 8H^+_{(aq)} + 2NO^-_{3(aq)} \rightarrow 6Fe^{3+}_{(aq)} + 4H_2O_{(l)} + 2NO_{(g)}$

$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

(b) $H_2O_2 + 2H^+_{(aq)} \longrightarrow 2H_2O_{(l)} + 2\bar{e}$

(c) $X_{2(g)} \longrightarrow 2X^-_{(aq)}$ X = Cl or Br

(d) $MnO^-_{4(aq)} + 8H^+_{(aq)} + 5\bar{e} \longrightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$

(e) $Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6\bar{e} \longrightarrow 2Cr^{2+}_{(aq)} + 7H_2O_{(l)}$

(f) With nitrous acid.

$Fe^{2+}_{(aq)} + 2H^+_{(aq)} + NO^-_{2(aq)} \longrightarrow Fe^{3+}_{(aq)} + H_2O_{(l)} + NO_{(g)}$

$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$

$Fe^{3+} + \bar{e} \longrightarrow Fe^{2+}$

(a) Potassium iodide.

$2I^-_{(aq)} + 2Fe^{3+}_{(aq)} \longrightarrow 2Fe^{2+} + I_{2(aq)}$

(b) SO_2 or SO_3^{2-}

$SO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2SO_3 \rightleftharpoons 2H^+_{(aq)} + SO^{2-}_{3(aq)}$

$SO^{2-}_{3(aq)} + H_2O_{(l)} + 2Fe^{3+}_{(aq)} \longrightarrow SO^{2-}_{4(aq)} + 2H^+_{(aq)} + 2Fe^{2+}_{(aq)}$

(c) Boiling with Zn powder & titanium (III) chloride.

$2Fe^{3+}_{(aq)} + Zn_{(s)} \longrightarrow 2Fe^{2+}_{(aq)} + Zn^{2+}_{(aq)}$

$Fe^{3+}_{(aq)} + Ti^{3+}_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + Ti^{4+}_{(aq)}$

(d) Hydrogen sulphide

$2Fe^{3+}_{(aq)} + S^{2-}_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + S_{(s)}$.

Examples

Cobalt

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$

Common oxidation states +2; +3.

Reactions

* Not affected by moist air at ordinary temp.
* At high temp reacts with oxygen to form cobalt(II) oxide and at lower temperatures to form ~~cobalt(III) oxide~~ tricobalt tetraoxide.

$2Co_{(s)} + O_{2(g)} \longrightarrow 2CoO_{(s)}$

$3Co_{(s)} + 2O_{2(g)} \longrightarrow Co_3O_{4(s)}$

* React with non metals on heating

$Co_{(s)} + Cl_{2(g)} \longrightarrow CoCl_{2(s)}$

$Co_{(s)} + Br_{2(l)} \longrightarrow CoBr_{2(s)}$

$3Co_{(s)} + 2P_{(s)} \longrightarrow Co_3P_{2(s)}$

$Co_{(s)} + S_{(s)} \longrightarrow CoS_{(s)}$

$2Co_{(s)} + C_{(s)} \longrightarrow Co_2C_{(s)}$

Reaction with acids

dilute HCl & H_2SO_4 ⇒ liberate $H_{2(g)}$ and form a corresponding salt. Rxn is slow.

$Co_{(s)} + 2H^+_{(aq)} \longrightarrow Co^{2+}_{(aq)} + H_{2(g)}$

conc. nitric acid renders the metal passive but reacts with dilute nitric acid.

$Co_{(s)} + 4HNO_{3(aq)} \longrightarrow Co(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$

* cobalt doesn't react with alkali.

Compounds of cobalt

stable o.s +2.

+3 oxidation is thereby oxidising readily reduced to +2 o.s. But stable in presence of complexing agents eg NH_3, CN^- etc.

* +3 oxidises water ∴ Co^{2+} cannot exist in water.

Cobalt (II) cpds

* Anhydrous cobalt (II) cpds: blue
* $Co(H_2O)_6^{2+}$ — pink

① **CoO** $CoCO_3 \longrightarrow CoO + CO_{2(g)}$

$2Co(NO_3)_2 \longrightarrow 2CoO_{(s)} + 4NO_{2(g)} + O_{2(g)}$

② **$Co(OH)_2$** $Co^{2+}_{(aq)} + 2\bar{O}H \longrightarrow Co(OH)_{2(s)}$ ↓ Blue ppt.

↳ gradually changes pink/brown on standing due to aerial oxidation

$2Co(OH)_{2(s)} + \frac{1}{2}O_{2(g)} \longrightarrow Co_2O_3 \cdot H_2O_{(s)} + H_2O$

brown solid.

dissolves readily in dilute acids forming pink solution

$Co(OH)_2 + 2H^+_{(aq)} \longrightarrow Co^{2+}_{(aq)} + 2H_2O_{(l)}$

$Co(OH)_{2(s)} + 2H^+_{(aq)} + 4H_2O_{(l)} \longrightarrow Co(H_2O)_6^{2+}$
Pink

③ **CoS** ⇒ Black ppt.

$Co^{2+}_{(aq)} + S^{2-} \longrightarrow CoS_{(s)}$ & prepared by passing H_2S through a Co(II) salt in presence of aqueous ammonia and ammonium chloride.

* Solubility product of CoS is too high to be ppted in acidic solution, the presence of NH_3/NH_4Cl buffer to hydrogen ions in soln.

④ $CoCl_2$; $Co(NO_3)_2$; $CoSO_4$.

$Co_{(s)} + Cl_{2(g)} \longrightarrow CoCl_{2(s)}$

$CoO_{(s)} + H_2SO_4 \longrightarrow CoSO_4 + H_2O$

$CoCO_{3(s)} + 2HNO_3 \longrightarrow Co(NO_3)_2 + H_2O + CO_{2(g)}$

Addition of conc HCl

* dilute Co^{2+} is pink due to presence of $Co(H_2O)_6^{2+}$. When conc HCl is added solution turns blue due to formation of $CoCl_4^{2-}$ due to ligand exchange.

$Co(H_2O)^{2+}_{6(aq)} + 4Cl^-_{(aq)} \rightleftharpoons CoCl^{2-}_{4(aq)} + 6H_2O_{(l)}$
Pink / blue.

* Equilibrium shifts on right on increasing the [HCl] and temperature (drives away water as steam).

Complexes

Co(III) complexes more stable than Cobalt(II) complexes ∴ Co(II) readily oxidised to Co(III) complexes except $Co(H_2O)_6^{2+}$.

eg $CoCl_3(NH_3)_6$ ⇒ Can be analysed using $AgNO_3$ soln to obtain isomers. etc.

$Co(NH_3)_6^{3+}$; $Co(CN)_6^{3-}$ etc.

Aqueous chemistry of Co^{2+}

① NaOH ⇒ blue ppt insoluble in excess turns pink with exposure to air

$Co^{2+}_{(aq)} + 2\bar{O}H \longrightarrow Co(OH)_{2(s)}$

$Co(OH)_{2(s)} + \frac{1}{2}O_{2(g)} \longrightarrow Co_2O_3 \cdot H_2O_n + H_2O$

Pink / grey pink / brown ppt.

② NH_3 dilute: Blue ppt insoluble in excess and turns red on standing.

$Co^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Co(OH)_{2(s)}$.

conc: Blue ppt soluble in excess forming a red soln which turns yellow on standing

② $Co(OH)_{2(s)} + 6NH_{3(g)} \rightarrow Co(NH_3)_6^{2+} + 2OH^-$ ⇒

In air is oxidized to $Co(NH_3)_6^{3+}$ ⇒ yellow.

(3a) $Co(NH_3)_6^{2+} \longrightarrow Co(NH_3)_6^{3+} + e^-$

* Rxn can be effected by other oxidising agents eg H_2O_2.

③ Addition of conc HCl; Pink soln turns blue

$Co(H_2O)_{6(aq)}^{2+} + 4Cl^-_{(aq)} \rightleftharpoons CoCl_{4(aq)}^{2-} + 6H_2O$.

On dilution blue solution turns back to pink.

④ Potassium thiocyanate & Ammonium thiocyanate.

→ Blue solution formed which can be extracted in an alcohol → Blue soln occurs in the alcohol layer.

$Co^{2+}_{(aq)} + 4SCN^- \longrightarrow Co(SCN)_4^{2-}$
pink blue.

$Co(H_2O)_{6(aq)}^{2+} + 4SCN^- \longrightarrow Co(SCN)_{4(aq)}^{2-} + 6H_2O$.

⑤ KCN solution ⇒ Reddish brown ppt soluble in excess.

$Co^{2+}_{(aq)} + 2CN^-_{(aq)} \longrightarrow Co(CN)_{2(s)}$ Brown ppt

$Co(CN)_{2(s)} + 4CN^-_{(aq)} \longrightarrow Co(CN)_{6(aq)}^{4-}$

⑥ Addition of sulphide eg $(NH_4)_2S$ or H_2S ⇒ Black ppt insoluble in dilute HCl.

$Co^{2+}_{(aq)} + S^{2-}_{(aq)} \longrightarrow CoS$ black.

Nickel $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$.

O.S ⇒ +2 (stable); +3 (rare).

* Aqueous solution appear green due to $Ni(H_2O)_6^{2+}$ ions.

NiO ⇒ green solid which is basic — insoluble in excess.

$Ni(OH)_2$ ⇒ green solid formed when NaOH soln is added. soluble in ammonia forming a blue soln due to $Ni(H_2O)_2(NH_3)_4^{2+}$ and $Ni(NH_3)_6^{2+}$.

Complexes of Ni

$Ni(H_2O)_6^{2+}$ – green $Ni(NH_3)_6^{2+}$ deep blue.

$Ni(CN)_4^{2-}$ · orange $NiCl_4^{2-}$ – blue, $Ni(CO)_4$ – oxidation state of Ni is zero; Tetra carbonyl nickel(0).

* Nickel dimethylglyoxime = Red ppt when DMG is added to Ni^{2+} salt.

Aqueous chemistry

① NaOH ⇒ green ppt insoluble in excess

$Ni^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Ni(OH)_{2(s)}$

② Aqueous ammonia ⇒ green ppt soluble in excess forming blue soln.

$Ni^{2+}_{(aq)} + 2OH^- \longrightarrow Ni(OH)_{2(s)}$ Green ppt

$Ni(OH)_{2(s)} + 6NH_{3(aq)} \rightleftharpoons Ni(NH_3)_{6(aq)}^{2+} + 2OH^-_{(aq)}$
deep blue soln.

③ DMG ⇒ Add dilute ammonia soln until in excess followed by DMG ⇒ Red ppt.

$2DMG + Ni^{2+}_{(aq)} + 2OH^- \longrightarrow Ni(DMG)_{2(s)} + 2H_2O$.

④ sodium carbonate solution: Green ppt formed. $Ni^{2+}_{(aq)} + CO_3^{2-} \rightarrow NiCO_{3(s)}$

⑤ Ammonia sulphide ⇒ Black ppt formed.

$Ni^{2+}_{(aq)} + S^{2-}_{(aq)} \longrightarrow NiS_{(s)}$.

⑥ Potassium hexacyanoferrate (II) soln
Green ppt soluble in ammonia soln.

⑦ Potassium hexacyanoferrate (III) soln
Brown ppt.

⑧ Potassium cyanide soln ⇒ yellow green ppt soluble in excess.

⑨ 2-Naphthol ⇒ Brown ppt soluble in dilute HCl

Copper $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$; common O.S +1, +2

Cu^+ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
Cu^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$
} +1 O.S very unstable and disproportionates to copper + Cu^{2+}

$2Cu^+_{(aq)} \longrightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$.

Stability Cu^{2+}

* Cu^{2+} though with partially filled 3d orbital is more stable than Cu^+ which has a fully filled 3d orbital.
* since ions exist in compounds and aqueous solution then hydration and lattice energy have to be assessed.
* Copper (II) ions have greater charge density than Cu^+ and hence with higher hydration energy compared to Cu^+ have more stability in aqueous solutions forming hexaaqua copper (II) ions solution.

The extra energy required for second ionisation energy is compensated by the hydration energy so much that copper (I) ion loses an electron to become Cu^{2+} which then release the hydration energy.

* Lattice energy is dependent on high charge and small cationic radius, these make copper (II) compounds more stable than copper (I) compounds.

Occurrence
- $CuFeS_2$ – copper pyrites ← main ore.
- Cu_2S – copper glance
- Cu_2O – copper cuprite
- $CuCO_3 \cdot Cu(OH)_2$ – malachite.

Extraction

① Concentration by froth floatation
- mix ore with H_2O and pine oil
- Blow air into mixture to agitate it.
- copper containing particles collect in froth and are skimmed off; filtered and dried.

② Roasting ore
- ore roasted in air — Iron is oxidised to iron (II) oxide

$2CuFeS_2 + 4O_{2(g)} \longrightarrow Cu_2S_{(s)} + 2FeO_{(s)} + 3SO_{2(g)}$

* SO_2 is used in contact process.

③ Smelting ⇒ product of roasting is heated in a blast furnace with silica.

$FeO_{(s)} + SiO_2 \longrightarrow FeSiO_{3(l)}$ slag poured away.

④ Conversion to blister copper.

· Cu_2S is heated in air forming Cu_2O which react with Cu_2S to form copper.

$2Cu_2S_{(s)} + 3O_{2(g)} \longrightarrow 2Cu_2O_{(s)} + 2SO_{2(g)}$

$Cu_2S_{(s)} + 2Cu_2O_{(s)} \longrightarrow 6Cu_{(s)} + SO_{2(g)}$.

⑤ Purification of copper (refining copper).

- Impurities in blister copper = Fe, S, ∴ has to be purified by electrolysis to form pure copper.
- Crude metal is made anode while pure Cu is cathode and electrolyte acidified copper(II) sulphate solution.

* Copper is deposited at cathode, leaving impurities at the anode.

$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$.

Reactions

* No reaction with water or steam but reacts with moist air forming basic copper (II) carbonate.

$CuCO_3 \cdot Cu(OH)_2 \cdot nH_2O$

* Reacts with oxygen on heating to form copper oxides

$2Cu_{(s)} + O_{2(g)} \longrightarrow 2CuO_{(s)}$

$4Cu_{(s)} + O_{2(g)} \longrightarrow 2Cu_2O_{(s)}$.

* Reacts with halogen on heating to form copper(II) halides except I_2 which form copper(I) iodide.
* Reactions with acids

(i) No reaction with non oxidising acids (dil HCl, H_2SO_4) except in presence of O_2 or oxidising agent

(ii) boiling conc HCl reacts with copper forming a complex

$2Cu_{(s)} + 2H^+_{(aq)} \longrightarrow 2Cu^{+}_{(aq)} + H_{2(g)}$

$Cu^+_{(aq)} + 2Cl^-_{(aq)} \rightleftharpoons CuCl_2^-{}_{(aq)}$.

(iii) Hot conc H_2SO_4 ⇒ liberates SO_2

$Cu_{(s)} + 2H_2SO_{4(l)} \longrightarrow CuSO_{4(aq)} + 2H_2O_{(l)} + SO_{2(g)}$

(iv) HNO_3

dil: $3Cu_{(s)} + 8HNO_{3(aq)} \longrightarrow 3Cu(NO_3)_{2(aq)} + 4H_2O_{(l)} + 2NO_{(g)}$

conc: $Cu_{(s)} + 4HNO_{3(aq)} \longrightarrow Cu(NO_3)_{2(aq)} + 2H_2O_{(l)} + 2NO_{2(g)}$

* Reacts with sulphur on heating.

$Cu_{(s)} + S_{(s)} \longrightarrow Cu_2S_{(s)}$.

Compounds of copper (I)

① Cu_2O

$Cu_2O_{(s)} + H_2SO_{4(aq)} \longrightarrow CuSO_{4(aq)} + Cu_{(s)} + H_2O_{(l)}$

$3Cu_2O_{(s)} + 14HNO_{3(aq)} \longrightarrow 6Cu(NO_3)_{2(aq)} + 7H_2O_{(l)} + 2NO_{(g)}$

conc HCl → complex formed

$Cu_2O_{(s)} + 2HCl_{(aq)} \longrightarrow 2CuCl_{(s)} + H_2O$

$CuCl_{(s)} + Cl^-_{(aq)} \longrightarrow CuCl_2^-{}_{(aq)}$ dark brown

Easily reduced

$Cu_2O_{(s)} + H_{2(g)} \longrightarrow 2Cu_{(s)} + H_2O_{(l)}$

$Cu_2O_{(s)} + C_{(s)} \longrightarrow 2Cu_{(s)} + CO_{(g)}$.

② CuCl soluble in ~~and~~ conc HCl and aqueous ammonia

$CuCl_{(s)} + Cl^- \rightleftharpoons CuCl_2^-{}_{(aq)}$

$CuCl_{(s)} + 2NH_3 \rightleftharpoons Cu(NH_3)_2^+{}_{(aq)}$

It dimerises at 1300K to form Cu_2Cl_2.

③ CuI ⇒ White solid precipitated when aqueous soln of copper(II) sulphate is added to an aqueous solution of KI

$2Cu^{2+}_{(aq)} + 4I^-_{(aq)} \longrightarrow Cu_2I_{2(s)} + I_{2(aq)}$

$2Cu^{2+}_{(aq)} + 4I^-_{(aq)} \longrightarrow 2CuI_{(s)} + I_{2(aq)}$.

Estimation of % of copper in an ore

* Known mass of ore is reacted with conc H_2SO_4 and resultant solution diluted to 250cm³ in a volumetric flask
* Portions are pipetted into a conical flask and an excess 10% potassium iodide solution added

$Cu^{2+}_{(aq)} + 4I^-_{(aq)} \longrightarrow Cu_2I_{2(s)} + I_{2(aq)}$.

* Liberated iodine is titrated with standard $Na_2S_2O_3$ using starch indicator

$2S_2O_3^{2-}{}_{(aq)} + I_{2(aq)} \longrightarrow S_4O_6^{2-}{}_{(aq)} + 2I^-_{(aq)}$.

* Through backward calculation, concentration of copper in 250cm³ can be calculated. Mass of copper can be determined and hence % of copper can be calculated.

$\% = \frac{\text{mass of Cu}}{\text{mass of ore}} \times 100$

Copper (II) compounds

$Cu(H_2O)_6^{2+}$ ion = Blue in aqueous solution

* solutions acidic due to hydrolysis.

① CuO = Black = $CuCO_{3(s)} \longrightarrow CuO_{(s)} + CO_{2(g)}$

decomposes at 800°C $4CuO_{(s)} \longrightarrow 2Cu_2O_{(s)} + O_{2(g)}$

Readily reduced by hydrogen $CuO_{(s)} + H_{2(g)} \longrightarrow Cu_{(s)} + H_2O_{(l)}$

typical basic oxides ⇒ $CuO_{(s)} + 2H^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + H_2O_{(l)}$

② $Cu(OH)_2$ ⇒ Pale blue solid $Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_{2(s)}$

dissolves in aqueous ammonia to form deep blue solution

$Cu(OH)_{2(s)} + 4NH_{3(aq)} \longrightarrow Cu(NH_3)_4^{2+}{}_{(aq)} + 2OH^-_{(aq)}$.

Readily reacts with acids $Cu(OH)_{2(s)} + 2H^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2H_2O$

decomposes on heating $Cu(OH)_{2(s)} \longrightarrow CuO_{(s)} + H_2O_{(g)}$.

③ $CuCl_2$ ⇒ dissolves in conc HCl to form a ~~bn~~ brownish yellow solution which on dilution turns green blue and finally pale blue.

* Conc HCl contains a high concentration of Cl^- ions which react with $CuCl_2$ forming yellow tetrachlorocuprate ion

$Cu^{2+}_{(aq)} + 4Cl^-_{(aq)} \rightleftharpoons [CuCl_4]^{2-}_{(aq)}$.

* on dilution the Cl^- ligands are replaced by H_2O ligands to form hexaaqua copper(II) ions which are blue

$CuCl_4^{2-}{}_{(aq)} + 6H_2O_{(l)} \rightleftharpoons Cu(H_2O)_6^{2+}{}_{(aq)} + 4Cl^-_{(aq)}$

NB: Copper (II) iodide doesn't exist because I_2 is not a powerful oxidising agent to oxidise copper (I) to copper (II) ∴ any attempt yields copper (I) iodide.

④ Copper (II) sulphate · $5H_2O$

$CuSO_4 \cdot 5H_2O_{(s)} \longrightarrow CuSO_4 \cdot H_2O_{(s)} + 4H_2O_{(l)}$ 100°C

$CuSO_4 \cdot H_2O_{(s)} \longrightarrow CuSO_4 + H_2O_{(g)}$ 250°C

$CuSO_{4(s)} \longrightarrow CuO_{(s)} + SO_{3(g)}$ 700°C

⑤ $CuCO_3$ ⇒ insoluble in water but soluble in aqueous ammonia due to complex formation

$CuCO_{3(s)} \rightleftharpoons Cu^{2+}_{(aq)} + CO_3^{2-} \xrightleftharpoons{4NH_3} Cu(NH_3)_4^{2+}{}_{(aq)}$

⑥ CuS ⇒ Black solid; $Cu^{2+}_{(aq)} + S^{2-}_{(aq)} \longrightarrow CuS_{(s)}$

~~$CuS + 2O_2 \longrightarrow CuSO_4$ Black solid turns white in moist air~~

$2CuS_{(s)} \longrightarrow Cu_2S_{(s)} + S_{(s)}$ → strong heating.

⑦ $Cu(NO_3)_2$

$2Cu(NO_3)_2 \longrightarrow 2CuO_{(s)} + 4NO_{2(g)} + O_{2(g)}$

Aqueous chemistry of copper (II) ions

① NaOH ⇒ Blue ppt insoluble in excess

$Cu^{2+}_{(aq)} + 2OH^- \longrightarrow Cu(OH)_{2(s)}$ ppt when heated turns black

$Cu(OH)_{2(s)} \longrightarrow CuO_{(s)} + H_2O_{(l)}$.

② $NH_{3(aq)}$ → Blue ppt soluble in excess forming deep blue solution

$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Cu(OH)_{2(s)}$ $Cu(OH)_{2(s)} + 4NH_{3(aq)} \longrightarrow Cu(NH_3)_4^{2+}{}_{(aq)} + 2OH^-$

③ Potassium hexacyanoferrate (II) solution.

$2Cu^{2+}_{(aq)} + Fe(CN)_6^{4-}{}_{(aq)} \longrightarrow CuFe(CN)_6$

* ~~Black ppt~~ Brown ppt soluble in ammonia solution.

④ Potassium iodide solution

White ppt stained brown which turns white on adding sodium thiosulphate

$2Cu^{2+}_{(aq)} + 4I^-_{(aq)} \longrightarrow Cu_2I_{2(s)} + I_{2(aq)}$

$2S_2O_3^{2-}{}_{(aq)} + I_{2(aq)} \longrightarrow S_4O_6^{2-}{}_{(aq)} + 2I^-_{(aq)}$.

⑤ Ammonium thiocyanate solution = Green solution

⑥ Ammonium sulphide or H_2S ⇒ Black solid

$Cu^{2+}_{(aq)} + S^{2-}_{(aq)} \longrightarrow CuS_{(s)}$

⑦ Na_2CO_3 ⇒ Green ppt $Cu^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \longrightarrow CuCO_{3(s)}$.

⑧ Conc HCl ⇒ blue solution turns yellow which on dilution turns blue again.

$Cu(H_2O)_6^{2+}{}_{(aq)} + 4Cl^-_{(aq)} \rightleftharpoons CuCl_4^{2-}{}_{(aq)} + 6H_2O_{(l)}$

yellow

Zinc $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

O'S +2

Reactions

① Reacts with O_2 on heating

$2Zn_{(s)} + O_{2(g)} \rightarrow 2ZnO_{(s)}$

② H_2O ⇒ No reaction with cold water but reacts with steam to form ZnO

$Zn_{(s)} + H_2O_{(g)} \rightarrow ZnO_{(s)} + H_{2(g)}$

③ Acids

*Dilute non oxidising acids (dilute HCl, H_2SO_4)

$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$.

*Conc H_2SO_4 $Zn_{(s)} + 2H_2SO_{4(l)} \rightarrow ZnSO_{4(aq)} + 2H_2O_{(l)} + SO_{2(g)}$

*Nitric acid ⇒ product depends on concentration and temperature.

$NO^-_{3(aq)} + 2H^+_{(aq)} + \bar{e} \rightarrow NO_{2(g)} + H_2O_{(l)}$

$NO^-_{3(aq)} + 10H^+_{(aq)} + 8\bar{e} \rightarrow NH^+_{4(aq)} + 3H_2O_{(l)}$

$NO^-_{2(aq)} + 4H^+_{(aq)} + 3\bar{e} \rightarrow NO_{(g)} + 2H_2O_{(l)}$

Combine with

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\bar{e}$

*Conc H_2SO_4

$4Zn_{(s)} + 5H_2SO_{4(l)} \rightarrow 4ZnSO_{4(aq)} + 4H_2O_{(l)} + H_2S_{(g)}$

$2H_2S_{(g)} + SO_{2(g)} \rightleftharpoons 2H_2O_{(l)} + 3S_{(s)}$

④ caustic aqueous alkali & Hot concentrated NaOH.

$Zn_{(s)} + 2\bar{O}H_{(aq)} + 2H_2O_{(l)} \rightarrow Zn(OH)^{2-}_{4(aq)} + H_{2(g)}$

$Zn_{(s)} + 2\bar{O}H_{(aq)} \rightarrow ZnO^{2-}_{2(aq)} + H_{2(g)}$.

$Zn_{(s)} + 2\bar{O}H_{(aq)} + 4H_2O_{(l)} \rightarrow [Zn(OH)_4(H_2O)_2]^{2-}_{(aq)} + H_{2(g)}$

⑤ Reaction with salt solution.

→ fairly strongly electropositive.

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

$Zn_{(s)} + Pb^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Pb_{(s)}$

⑥ Non metals ⇒ React on heating

$Zn_{(s)} + Cl_{2(g)} \rightarrow ZnCl_{2(s)}$

$Zn_{(s)} + S_{(s)} \rightarrow ZnS_{(s)}$

$3Zn_{(s)} + N_{2(g)} \rightarrow \cancel{3}Zn_3N_2$

Compounds of Zn

*O.S +2; aqueous solution $Zn(H_2O)^{2+}_{2(aq)}$
Not transitional because

→ Zinc atom has a full 3d-orbital.

→ Has only +2 O.S with fully filled 3d orbital.

→ compounds are white or colourless since 3d orbital full

→ Not paramagnetic since all 3d-electrons paired.

Transition properties

*forms several complexes; with coordination No of 4 and tetrahedral e.g. $Zn(OH)_4^{2-}$; $Zn(H_2O)_4^{2+}$; $Zn(CN)_4^{2-}$ $Zn(NH_3)_4^{2+}$; $ZnCl_4^{2-}$ etc.

① ZnO ⇒ White solid; yellow when hot; amphoteric

$ZnO_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_2O_{(l)}$

dissolves in aqueous ~~ammonia~~ sodium hydroxide

$ZnO_{(s)} + 2\bar{O}H_{(aq)} + H_2O_{(l)} \rightleftharpoons Zn(OH)^{2-}_{4(aq)}$

$ZnO_{(s)} + 2\bar{O}H_{(aq)} \rightleftharpoons ZnO^{2-}_{2(aq)} + H_2O_{(l)}$.

Reduced by C or CO

$2ZnO_{(s)} + C_{(s)} \rightarrow 2Zn_{(s)} + CO_{2(g)}$

$ZnO_{(s)} + CO_{(g)} \rightleftharpoons Zn_{(s)} + CO_{2(g)}$.

② $Zn(OH)_2$ - White ppt

$Zn^{2+}_{(aq)} + 2\bar{O}H_{(aq)} \rightarrow Zn(OH)_{2(s)}$.

amphoteric

$Zn(OH)_{2(s)} + 2H^+_{(aq)} \rightarrow Zn_{(s)} + 2H_2O_{(l)}$

concentrated alkali to form zincate ion.

$Zn(OH)_{2(s)} + 2\bar{O}H_{(aq)} \rightarrow Zn(OH)^{2-}_{4(aq)}$

$Zn(OH)_{2(s)} + 2\bar{O}H_{(aq)} \rightarrow ZnO^{2-}_{2(aq)} + 2H_2O_{(l)}$

dissolves in aqueous ammonia

$Zn(OH)_{2(s)} + 4NH_{3(aq)} \rightarrow Zn(NH_3)^{2+}_{4(aq)} + 2\bar{O}H_{(aq)}$

$Zn(OH)_2$ pptd by ammonia when added with ammonium chloride

③ ZnS pptates readily if H_2S passed thro' a Zn^{2+} ions solution buffered by ammonium chloride.

$Zn^{2+}_{(aq)} + H_2S_{(g)} \rightarrow ZnS_{(s)} + 2H^+$ White

*Passing H_2S into a soln precipitates metallic sulphides but in acidic conditions no precipitates formed because H+ suppress the ionisation of H_2S.

$H_2S_{(aq)} \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}$.

*This lowers the $[S^{2-}]$ ions in solution; only sulphides with low Ksp can be precipitated eg CuS but not ZnS.

*This explains explains why buffering is necessary to eliminate H+ or to shift the ionisation equilibrium to right forming more sulphide.

④ $ZnCl_2$

Heating $ZnCl_2 \cdot 2H_2O$ forms anhydrous $ZnCl_2$ unlike $MgCl_2$ which undergoes hydrolysis on heating.

*soluble in organic solvents since its covalent.

⑤ $ZnCO_3$ ⇒ White solid.

Formed by addition of $NaHCO_3$ to Zn^{2+}.

$Zn^{2+}_{(aq)} + 2HCO^-_{3(aq)} \rightarrow ZnCO_{3(s)} + CO_{2(g)} + H_2O_{(l)}$

However addition Na_2CO_3 gives a white ppt of $Zn(OH)_{2(s)}$ because Na_2CO_3 is more alkaline than $NaHCO_3$.

Aqueous chemistry of Zn^{2+}

① Aqueous NaOH ⇒ White ppt. soluble in excess to form colourless soln

$Zn^{2+}_{(aq)} + 2\bar{O}H_{(aq)} \rightarrow Zn(OH)_{2(s)}$; $Zn(OH)_{2(s)} + 2\bar{O}H_{(aq)} \rightarrow Zn(OH)^{2-}_{4(aq)}$

$Zn(OH)_{2(s)} + 2\bar{O}H_{(aq)} \rightarrow ZnO^{2-}_{2(aq)} + 2H_2O_{(l)}$

② Aq NH_3 ⇒ White ppt soluble in excess

$Zn^{2+}_{(aq)} + 2\bar{O}H_{(aq)} \rightarrow Zn(OH)_{2(s)}$; $Zn(OH)_{2(s)} + 4NH_{3(aq)} \rightleftharpoons Zn(NH_3)^{2+}_4 + 2\bar{O}H_{(aq)}$

③ Potassium hexacyanoferrate (II) solution.

White ppt soluble in sodium hydroxide

$2Zn^{2+}_{(aq)} + Fe(CN)^{4-}_{6(aq)} \rightarrow Zn_2FeCN_{6(s)}$

④ Potassium hexacyanoferrate (III) solution

Yellow ppt. Insoluble in ammonia

$3Zn^{2+}_{(aq)} + 2Fe(CN)^{3-}_{6(aq)} \rightarrow Zn_3(Fe(CN)_6)_2$

⑤ Addition of disodium hydrogen phosphate.

*Add solid NH_4Cl, followed by drops of Na_2HPO_4 and then add ammonia solution in excess.

$Zn^{2+}_{(aq)} + NH^+_{4(aq)} + HPO^{2-}_{4(aq)} \rightarrow ZnNH_4PO_4 + H^+_{(aq)}$