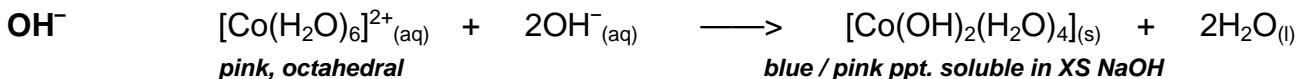


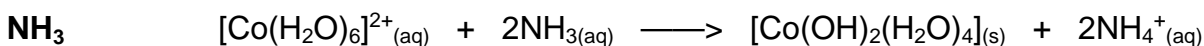
REACTIONS OF SOME TRANSITION METAL IONS

COBALT

- Cobalt(II)**
- aqueous solutions contain the **pink, octahedral** hexaaquacobalt(II) ion.
 - hexaaqua ions can also be present in solid samples of the hydrated salts.
 - as it is a 2+ ion, the solutions are weakly acidic but protons can be removed by bases...

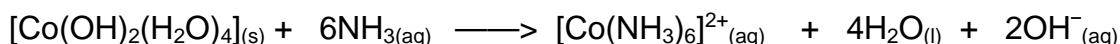


ALL hexaaqua ions precipitate a hydroxide with $\text{OH}^-_{(\text{aq})}$. Some redissolve in excess NaOH.

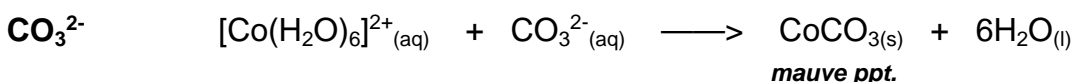
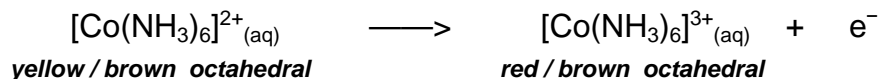


ALL hexaaqua ions precipitate a hydroxide with $\text{NH}_3_{(\text{aq})}$. It removes protons.

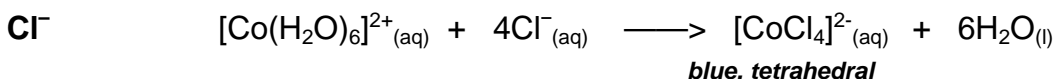
Some hydroxides redissolve in excess $\text{NH}_{3(\text{aq})}$ as ammonia substitutes as a ligand.



but ... ammonia ligands make the Co(II) state unstable. Air oxidises Co(II) to Co(III).



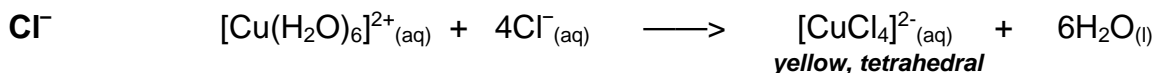
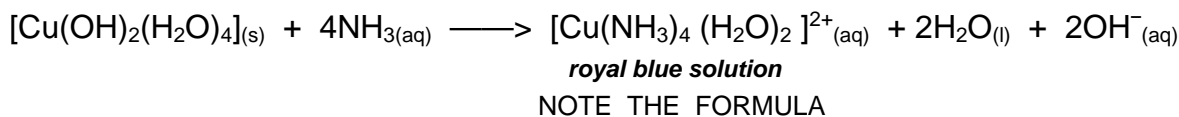
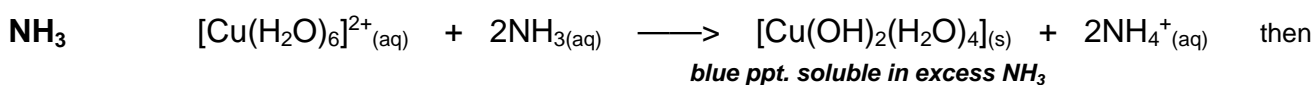
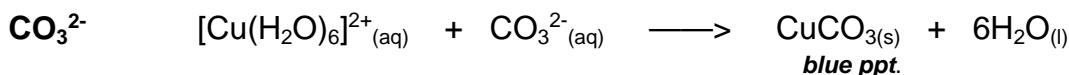
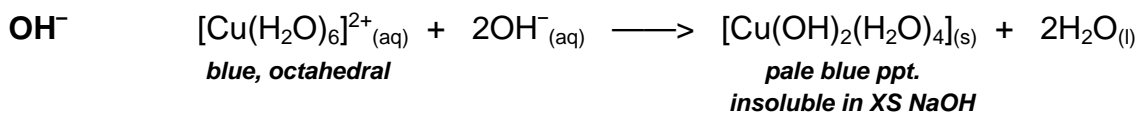
ALL hexaaqua ions of metals with charge 2+ precipitate a carbonate but 3+ ones don't.



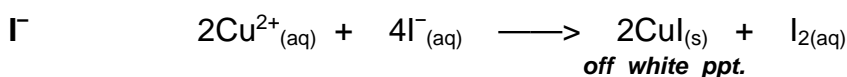
- Cl^- ligands are larger than H_2O and are charged
- the complex is more stable if the shape changes to tetrahedral - less repulsion between ligands
- adding excess water reverses the reaction

COPPER

Copper (II) Aqueous solutions of copper(II) contain the **blue, octahedral** hexaaquacopper(II) ion. Most substitution reactions are similar to cobalt(II).

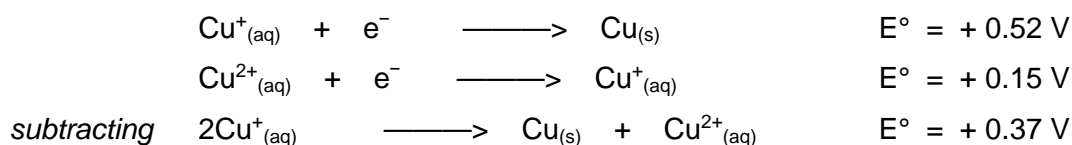


- Cl⁻ ligands are larger than H₂O and are charged
- the complex is more stable if the shape changes to tetrahedral
- adding excess water reverses the reaction



- a **redox** reaction
- used in the volumetric analysis of copper using sodium thiosulphate

Copper(I) The aqueous chemistry of copper(I) is unstable with respect to copper(0) and copper (II).



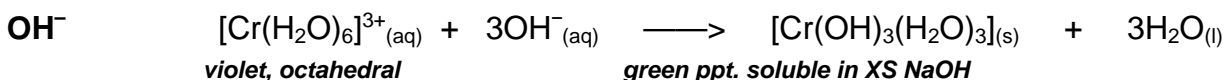
DISPROPORTIONATION:- a species is simultaneously oxidised and reduced to more stable forms. This explains why the aqueous chemistry of copper(I) is very limited.

Stabilisation Copper(I) can be stabilised by forming complexes **[Cu(NH₃)₂]⁺** **[Cu(CN)₂]⁻**

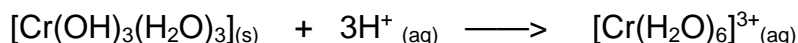
USES Copper is used in alloys such as brass and bronze

CHROMIUM

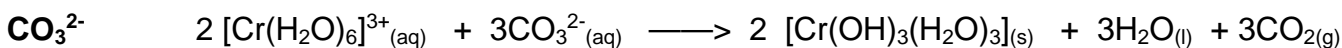
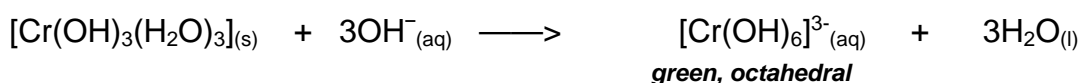
Chromium(III) Chromium(III) ions are typical of M^{3+} ions in this block.
Aqueous solutions contain the violet, octahedral hexaaquachromium(III) ion.



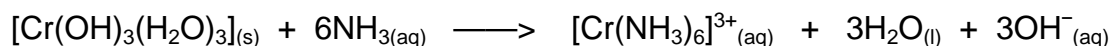
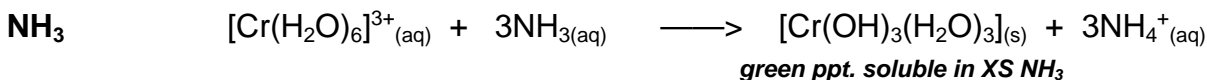
As with all hydroxides the precipitate reacts with acid



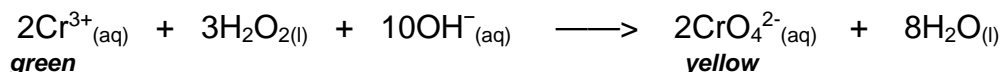
being a 3+ hydroxide it is AMPHOTERIC as it dissolves in excess alkali



The carbonate is not precipitated but the hydroxide is. The high charge density of M^{3+} ions makes the solutions too acidic to form the carbonate. CARBON DIOXIDE IS EVOLVED.

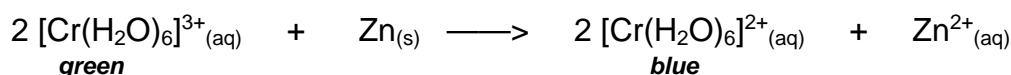


Oxidation In the presence of alkali, Cr(III) is unstable and can be **oxidised** to Cr(VI) with peroxide.



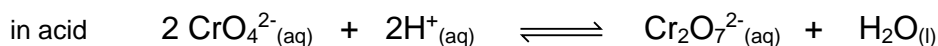
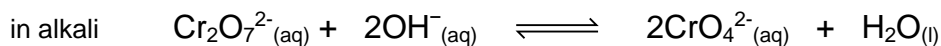
Acidification of the yellow chromate will produce the orange dichromate(VI) ion

Reduction Chromium(III) can be reduced to the less stable chromium(II) by zinc in acidic solution.



Chromium (VI)	Occurs as	dichromate (VI)	$\text{Cr}_2\text{O}_7^{2-}$	orange
	and	chromate (VI)	CrO_4^{2-}	yellow

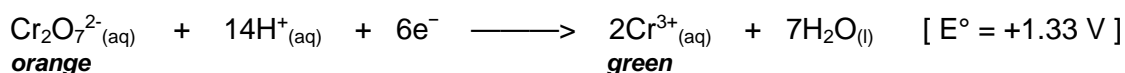
Interconversion **Dichromate is stable in acid solution; chromate is stable in alkaline solution.**



Oxidising power

Being in the highest oxidation state (+6), they will be oxidising agents.

In acidic solution, dichromate is widely used in both organic (oxidation of alcohols) and inorganic chemistry. It can also be used as a volumetric reagent but with special indicators as its colour change (orange to green) makes the end point hard to observe.

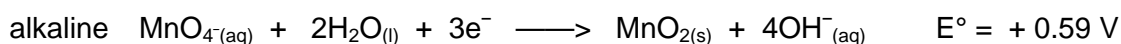
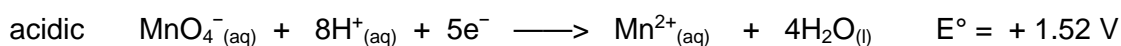


- Its E° value is lower than that of Cl_2 (1.36V) so can be used in the presence of Cl^- ions.
- MnO_4^- ($E^\circ = 1.52\text{V}$) oxidises chloride in HCl so must be acidified with sulphuric acid.
- Chromium(VI) can be reduced back to chromium(III) using zinc in acid solution.

MANGANESE

Mn (VII)

- Manganese is in its highest oxidation state therefore Mn(VII) will be an oxidising agent
- Occurs in the purple, tetraoxomanganate(VII) (permanganate) ion (MnO_4^-).
- It acts as an oxidising agent in acidic or alkaline solution.



N.B. Acidify with dilute H_2SO_4 NOT dilute HCl

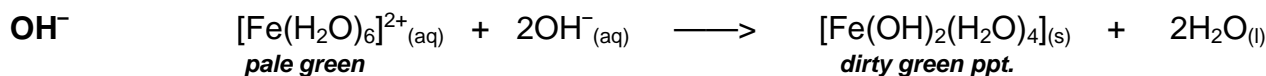
In volumetric analysis it must be acidified with dilute sulphuric acid as MnO_4^- is powerful enough to oxidise the chloride ions in hydrochloric acid.

It is used to estimate iron(II), hydrogen peroxide, ethanedioic (oxalic) acid and ethanedioate (oxalate) ions. The last two titrations are carried out above 60°C due to the slow rate of reaction.

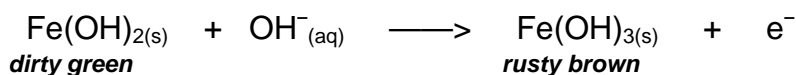
No indicator is required; the end point being the first sign of a permanent pale pink colour.

IRON

Iron (II) When iron reacts with acids it gives rise to iron(II) (ferrous) salts. Aqueous solutions of such salts contain the pale green, octahedral hexaaquairon(II) ion.



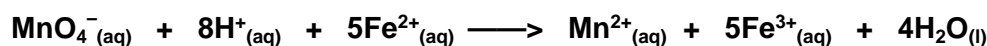
It only re-dissolves in very conc. OH^- but on standing in air it slowly turns a rusty brown colour due to oxidation to iron(III). Increasing the pH renders iron(II) unstable.



CO_3^{2-} Off-white coloured iron(II) carbonate, FeCO_3 , precipitated.

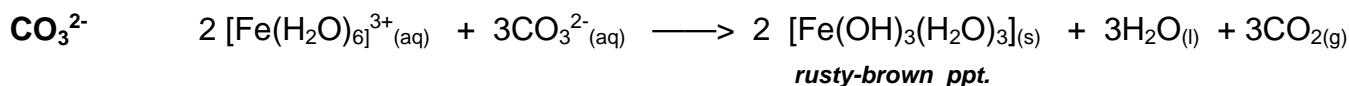
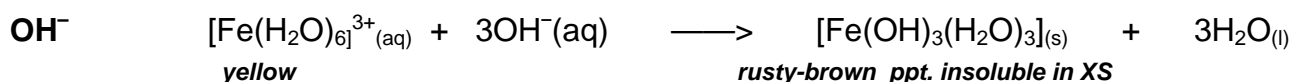
NH_3 Iron(II) hydroxide precipitated, insoluble in excess ammonia.

Volumetric Iron(II) can be analysed by titration with potassium manganate(VII) in acidic (H_2SO_4) solution. No indicator is required.

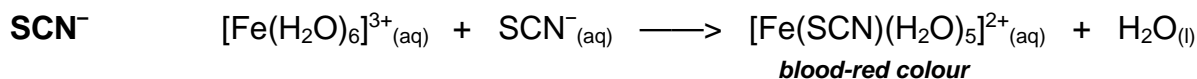
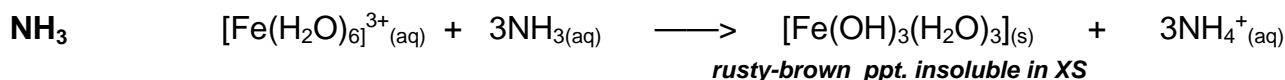


this means that $\frac{\text{moles of Fe}^{2+}}{\text{moles of MnO}_4^-} = \frac{5}{1}$

Iron(III) Aqueous solutions contain the yellow-green, octahedral hexaaquairon(III) ion. It behaves as a typical M^{3+} ion.



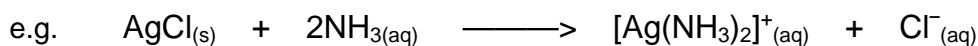
The carbonate is not precipitated but the hydroxide is. High charge density of M^{3+} ions makes the solutions too acidic to form the carbonate. CARBON DIOXIDE EVOLVED.



Very sensitive. A blood red colour confirms Fe(III). No reaction with Fe(II)

Silver (I)

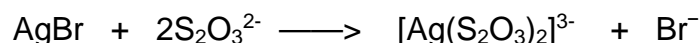
Occurrence The diammine silver(I) ion is formed when ammonia dissolves silver halides



see notes on identification of halide ions in solution

Complexes Silver(I) complexes are **colourless in aqueous solution** and tend to be **linear**.

[Ag(SO₃)₂]³⁻ Formed when silver salts are dissolved in sodium thiosulphate "hypo" solution. The reaction is important in photographic fixing; silver bromide which has not been exposed to light is dissolved away leaving the black image of silver as the negative.



[Ag(CN)₂]⁻ Formed when silver salts are dissolved in sodium or potassium cyanide and the solution used for silver electroplating.

[Ag(NH₃)₂]⁺ • Used in Tollen's reagent (SILVER MIRROR TEST)

Tollen's reagent is used to differentiate between aldehydes and ketones. Aldehydes produce a silver mirror on the inside of the test tube.

• Formed when silver halides dissolve in ammonia - TEST FOR HALIDES

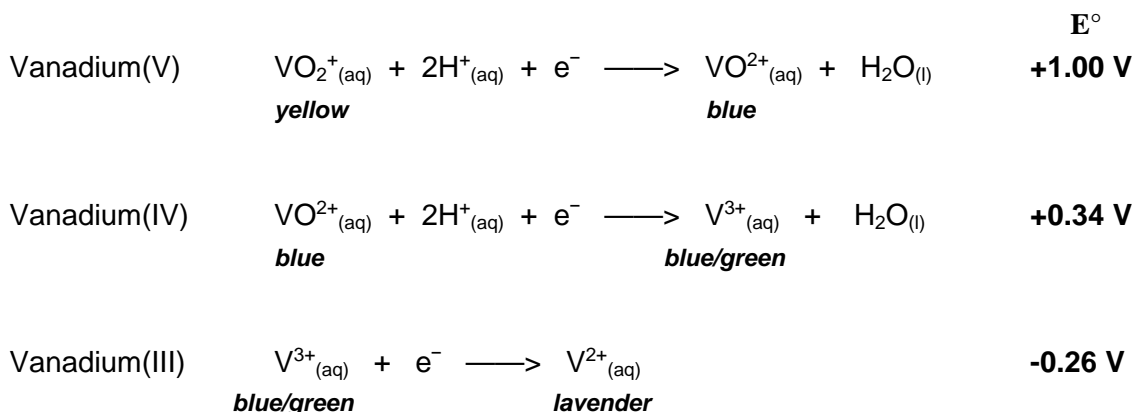
OTHER IMPORTANT COMPOUNDS INVOLVING COMPLEXES

Haemoglobin A complex containing iron(II) which is responsible for the red colour in blood and for the transport of oxygen by red blood cells.

Co-ordination of CO molecules interferes with the process

Cis-platin An important anti-cancer drug. It is a square planar, 4 co-ordinate complex of platinum.

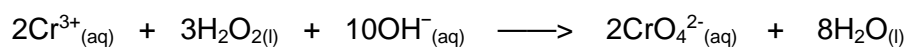
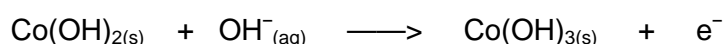
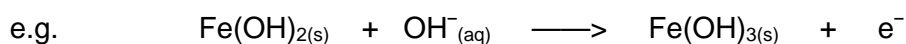
VANADIUM Reduction using zinc in acidic solution shows the various oxidation states of vanadium.



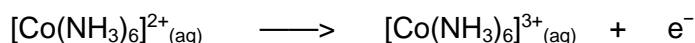
Uses V_2O_5 Vanadium(V) oxide is used as a catalyst in the CONTACT PROCESS
It has the ability to change its oxidation state

Oxidation and reduction of transition metal ions - Summary

- Oxidation**
- hexaaqua metal ions
 - are stable in acid solution
 - tend to be less stable in alkaline solution
 - in alkaline conditions they form neutral hydroxides and/or anionic complexes
 - it is easier to remove electrons from species which are neutral or negatively charged
 - conditions involve addition of **sodium hydroxide** followed by **hydrogen peroxide**



- Solutions of cobalt(II) can be oxidised by air under ammoniacal conditions

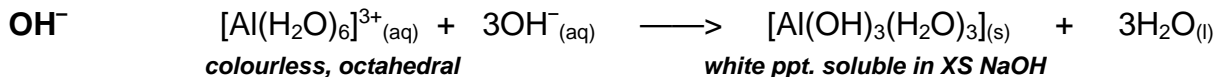


- Reduction**
- zinc metal is used to reduce transition metal ions to lower oxidation states
 - acts in acid solution as follows . . . $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$

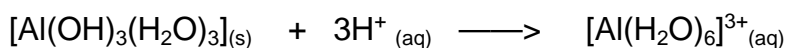
e.g. it reduces
 iron(III) to iron(II)
 vanadium(V) to vanadium (IV)
 vanadium(IV) to vanadium(III)

ALUMINIUM

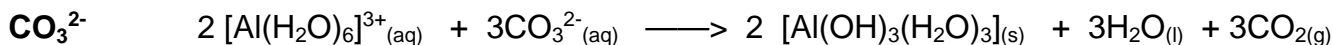
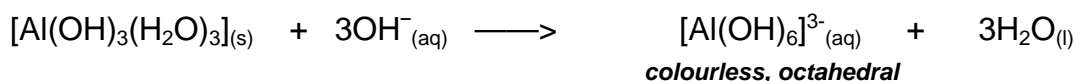
- Properties*
- aluminium is not a transition metal as it doesn't make use of d orbitals... *however*
 - due to their **high charge density**, aluminium(III) ions behave as typical M^{3+} ions
 - aqueous solutions contain the **colourless**, octahedral hexaaquaaluminium(III) ion



As with all hydroxides the precipitate reacts with acid



being a 3+ hydroxide it is AMPHOTERIC and dissolves in excess alkali



The carbonate is not precipitated but the hydroxide is. The high charge density of M^{3+} ions makes the solutions too acidic to form the carbonate. CARBON DIOXIDE IS EVOLVED.

