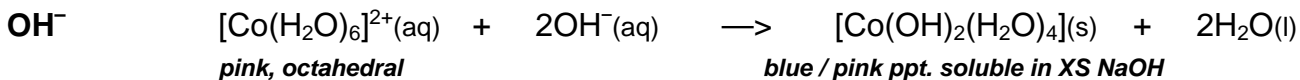


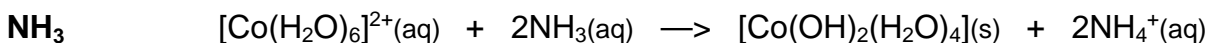
REACTIONS OF SOME TRANSITION METAL IONS

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.
 - solutions of 2+ ions are weakly acidic but protons can be removed by bases...

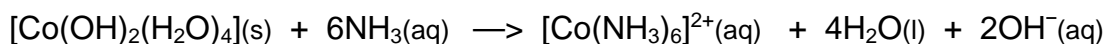


ALL hexaaqua ions precipitate a hydroxide with $\text{OH}^-(\text{aq})$. Some redissolve in excess NaOH.

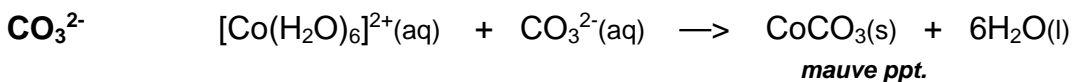
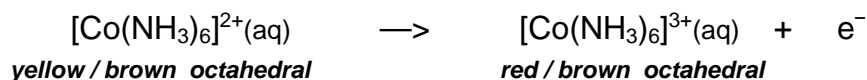


ALL hexaaqua ions precipitate a hydroxide with $\text{NH}_3(\text{aq})$. It removes protons.

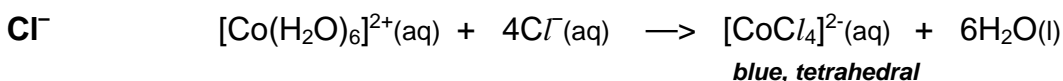
Some hydroxides dissolve in excess $\text{NH}_3(\text{aq})$ as ammonia substitutes as a ligand



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



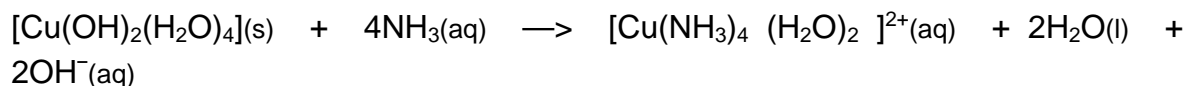
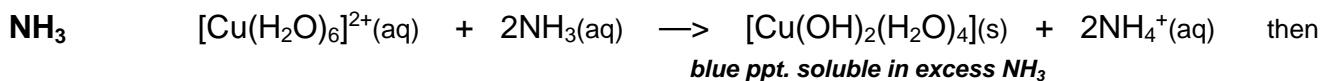
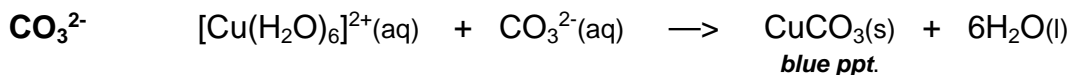
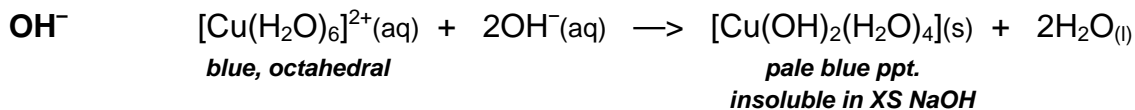
ALL hexaaqua ions of 2+ metal ions precipitate a carbonate; 3+ ones don't.



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

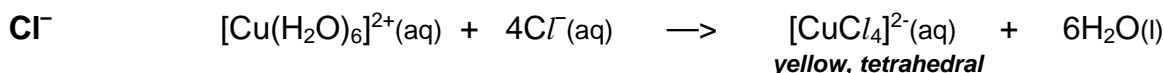
COPPER

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

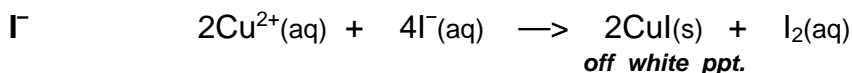


royal blue solution

NOTE THE FORMULA

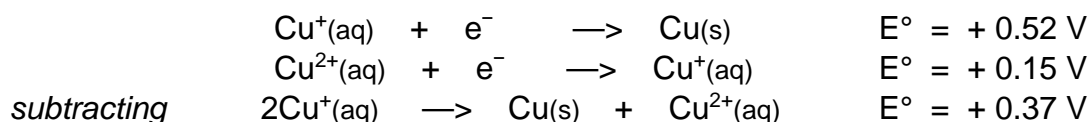


- Cl⁻ ligands are larger than H₂O and are charged
- the complex is more stable if the shape changes to tetrahedral
- adding excess water reverses the reaction



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

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



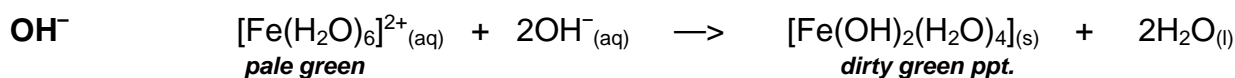
DISPROPORTIONATION:- a species is simultaneously oxidised and reduced
to more stable forms - explains why aqueous copper(I) chemistry is very limited.

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

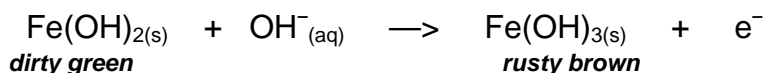
Uses Copper is used in alloys such as **BRASS** and **BRONZE**

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.



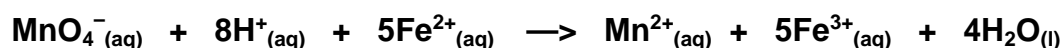
Re-dissolves in very conc. OH^- but **on standing in air it slowly turns rusty brown** due to oxidation to iron(III). Increasing the pH renders iron(II) unstable.



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

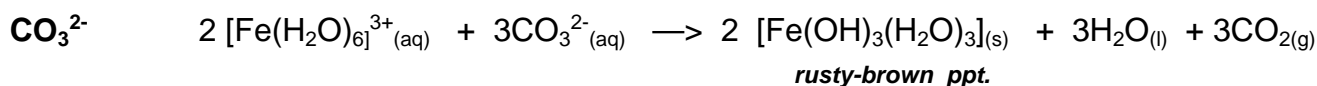
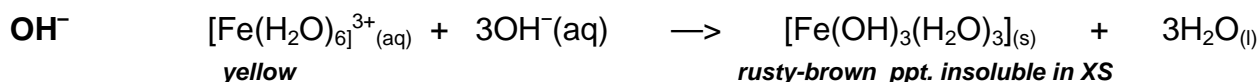
NH_3 Iron(II) hydroxide precipitated, insoluble in excess ammonia.

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

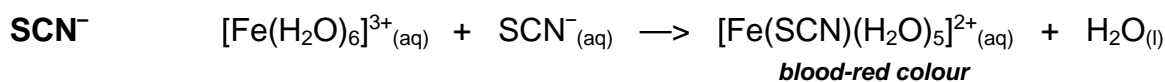
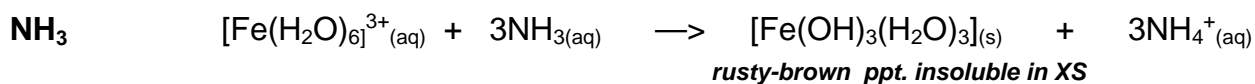


this means that $\frac{\text{moles of Fe}^{2+}}{\text{moles of MnO}_4^-} = \frac{5}{1}$

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



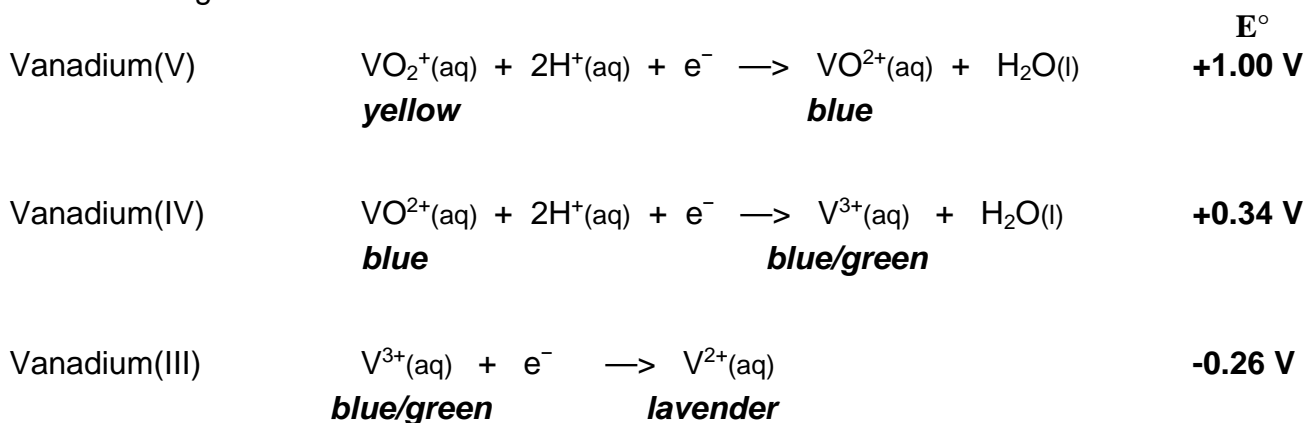
The carbonate is not precipitated but the hydroxide is. High charge density of M^{3+} ions makes the solutions too acidic to form the carbonate. **CARBON DIOXIDE EVOLVED.**



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

VANADIUM

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

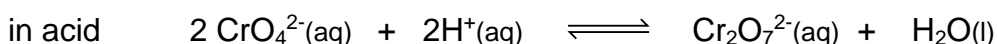
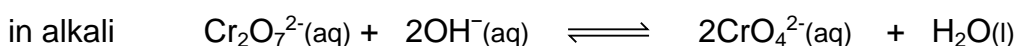


Uses V_2O_5 Vanadium(V) oxide is used as a catalyst in the CONTACT PROCESS
It has the ability to change its oxidation state

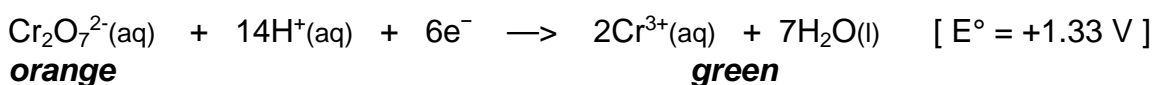
CHROMIUM

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.



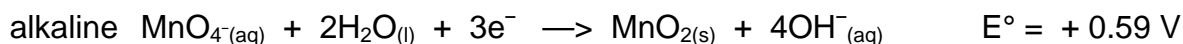
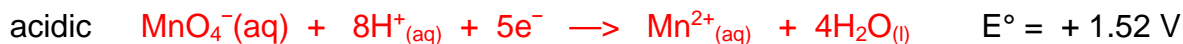
Oxidising power Being in the highest oxidation state (+6), they will be oxidising agents.
In acid, dichromate is widely used in both organic (oxidation of alcohols) and inorganic chemistry. It can be used as a volumetric reagent but with special indicators as its colour change (orange to green) makes the end point hard to observe.



- Its E° value is lower than Cl_2 (1.36V) so can be used in the presence of Cl^- ions
- MnO_4^- ($E^\circ = 1.52\text{V}$) oxidises Cl^- 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 so 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

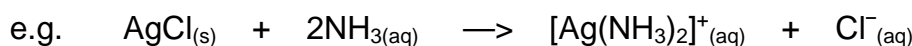
In volumetric analysis it must be acidified with dilute sulphuric acid as MnO_4^- is powerful enough to oxidise the chloride ions in hydrochloric acid.

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.

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**.

$[\text{Ag}(\text{NH}_3)_2]^+$ • 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

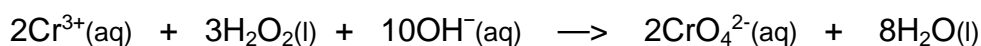
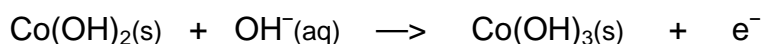
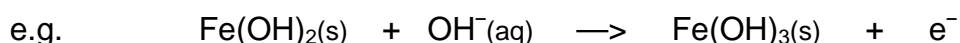
Haemoglobin A complex containing iron(II) which is responsible for the red colour in blood and for the transport of oxygen by red blood cells.

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.

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 neutral or negatively charged species
 - conditions - 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)