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...

OH⁻

$$[Co(H_2O)_6]^{2+}(aq) \ + \ 2OH^-(aq) \quad \longrightarrow \quad [Co(OH)_2(H_2O)_4](s) \ + \ 2H_2O(l)$$
       pink, octahedral   *blue / pink ppt. soluble in XS NaOH*
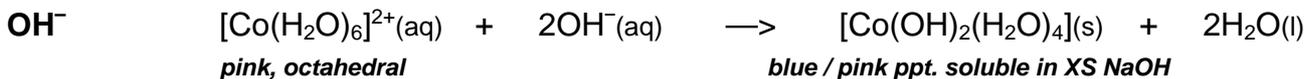
ALL hexaaqua ions precipitate a hydroxide with OH⁻(aq). Some redissolve in excess NaOH.

NH₃

$$[Co(H_2O)_6]^{2+}(aq) \ + \ 2NH_3(aq) \ \longrightarrow \ [Co(OH)_2(H_2O)_4](s) \ + \ 2NH_4^+(aq)$$
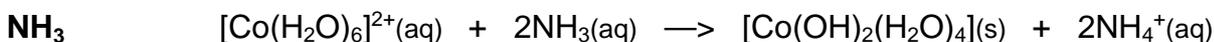
ALL hexaaqua ions precipitate a hydroxide with NH₃ (aq). It removes protons.

Some hydroxides dissolve in excess NH_3(aq) as ammonia substitutes as a ligand

$$[Co(OH)_2(H_2O)_4](s) \ + \ 6NH_3(aq) \ \longrightarrow \ [Co(NH_3)_6]^{2+}(aq) \ + \ 4H_2O(l) \ + \ 2OH^-(aq)$$

but ... ammonia ligands make the Co(II) state unstable. Air oxidises Co(II) to Co(III).
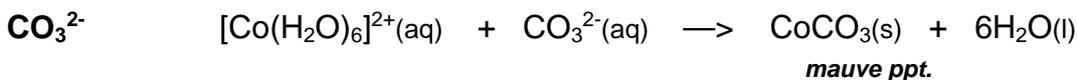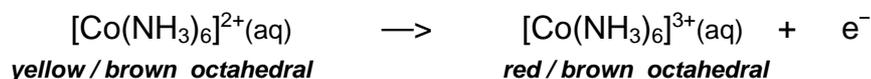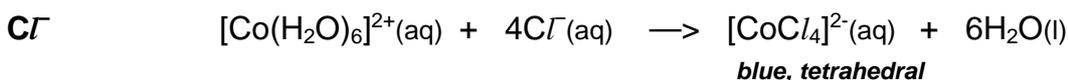
$$[Co(NH_3)_6]^{2+}(aq) \qquad \longrightarrow \qquad [Co(NH_3)_6]^{3+}(aq) \ + \ e^-$$
       yellow / brown octahedral   *red / brown octahedral*

CO₃²⁻

$$[Co(H_2O)_6]^{2+}(aq) \ + \ CO_3^{2-}(aq) \ \longrightarrow \ CoCO_3(s) \ + \ 6H_2O(l)$$
                                                          mauve ppt.

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

Cl⁻

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

• 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).
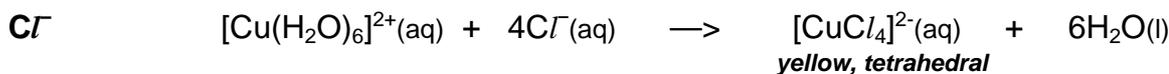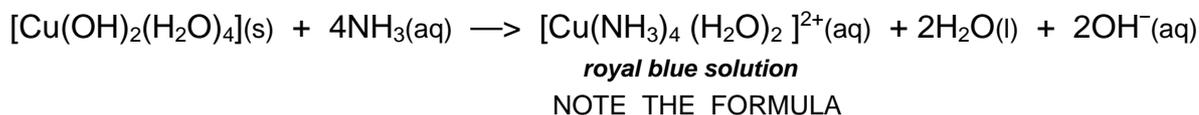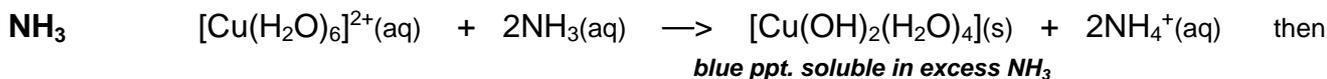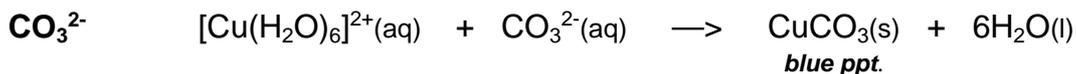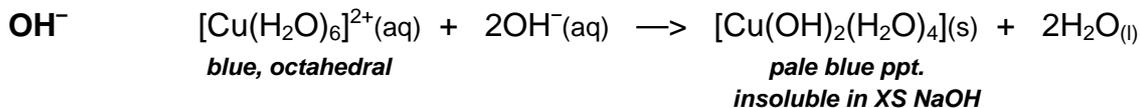
OH⁻ $[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \longrightarrow [Cu(OH)_2(H_2O)_4](s) + 2H_2O_{(l)}$
blue, octahedral   *pale blue ppt.*
insoluble in XS NaOH

CO₃²⁻ $[Cu(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CuCO_3(s) + 6H_2O(l)$
blue ppt.

NH₃ $[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \longrightarrow [Cu(OH)_2(H_2O)_4](s) + 2NH_4^+(aq)$ then
blue ppt. soluble in excess NH₃

$[Cu(OH)_2(H_2O)_4](s) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4 (H_2O)_2]^{2+}(aq) + 2H_2O(l) + 2OH^-(aq)$
royal blue solution
NOTE THE FORMULA

Cl⁻ $[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \longrightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)$
yellow, tetrahedral

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

I⁻ $2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow 2CuI(s) + I_2(aq)$
off white ppt.
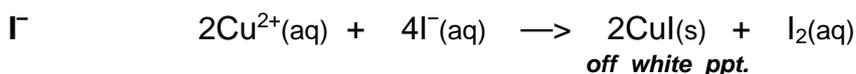
- a **redox** reaction
- used in the volumetric analysis of copper using sodium thiosulphate

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

$Cu^+(aq) + e^-$	$\longrightarrow$	$Cu(s)$	$E° = + 0.52$ V
$Cu^{2+}(aq) + e^-$	$\longrightarrow$	$Cu^+(aq)$	$E° = + 0.15$ V
subtracting $2Cu^+(aq)$	$\longrightarrow$	$Cu(s) + Cu^{2+}(aq)$	$E° = + 0.37$ V
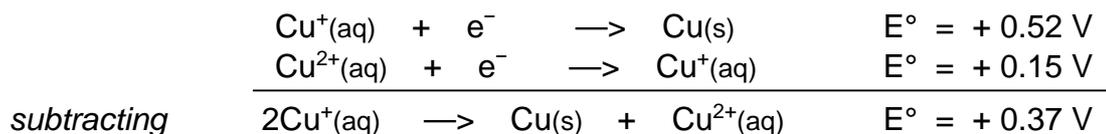
DISPROPORTIONATION:- a **species is simultaneously oxidised and reduced**
to more stable forms - explains why aqueous copper(I) chemistry is very limited.

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

Copper(0)   *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.

OH⁻ $[Fe(H_2O)_6]^{2+}_{(aq)}$ + $2OH^-_{(aq)}$ —> $[Fe(OH)_2(H_2O)_4]_{(s)}$ + $2H_2O_{(l)}$
   pale green   *dirty green ppt.*
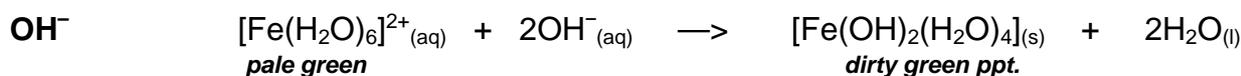
Re-dissolves in very conc. OH⁻ but **on standing in air it slowly turns rusty brown** due to oxidation to iron(III). Increasing the pH renders iron(II) unstable.

$Fe(OH)_{2(s)}$ + $OH^-_{(aq)}$ —> $Fe(OH)_{3(s)}$ + e^-
   dirty green   *rusty brown*
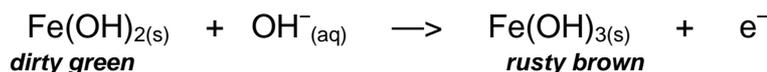
CO₃²⁻ Off-white coloured iron(II) carbonate, $FeCO_3$, precipitated.

NH₃ 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.

$MnO_4^-{}_{(aq)}$ + $8H^+_{(aq)}$ + $5Fe^{2+}_{(aq)}$ —> $Mn^{2+}_{(aq)}$ + $5Fe^{3+}_{(aq)}$ + $4H_2O_{(l)}$

this means that $\dfrac{\text{moles of } Fe^{2+}}{\text{moles of } MnO_4^-}$ = $\dfrac{5}{1}$

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

OH⁻ $[Fe(H_2O)_6]^{3+}_{(aq)}$ + $3OH^-(aq)$ —> $[Fe(OH)_3(H_2O)_3]_{(s)}$ + $3H_2O_{(l)}$
   yellow   *rusty-brown ppt. insoluble in XS*

CO₃²⁻ $2[Fe(H_2O)_6]^{3+}_{(aq)}$ + $3CO_3^{2-}{}_{(aq)}$ —> $2[Fe(OH)_3(H_2O)_3]_{(s)}$ + $3H_2O_{(l)}$ + $3CO_{2(g)}$
                                                 rusty-brown ppt.

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.

NH₃ $[Fe(H_2O)_6]^{3+}_{(aq)}$ + $3NH_{3(aq)}$ —> $[Fe(OH)_3(H_2O)_3]_{(s)}$ + $3NH_4^+{}_{(aq)}$
                                 rusty-brown ppt. insoluble in XS

SCN⁻ $[Fe(H_2O)_6]^{3+}_{(aq)}$ + $SCN^-_{(aq)}$ —> $[Fe(SCN)(H_2O)_5]^{2+}_{(aq)}$ + $H_2O_{(l)}$
                                            blood-red colour
   Very sensitive. A blood red colour confirms Fe(III). No reaction with Fe(II)

MANGANESE

Mn(II)
- solutions contain the **very pale pink, octahedral** hexaaquamanganese(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...

OH⁻

$$[Mn(H_2O)_6]^{2+}(aq) \;+\; 2OH^-(aq) \;\longrightarrow\; [Mn(OH)_2(H_2O)_4](s) \;+\; 2H_2O(l)$$

very pale pink, octahedral   *off-white pt.* **insoluble in XS NaOH**
darkens on standing due to oxidation

ALL hexaaqua ions precipitate a hydroxide with OH⁻(aq). Some redissolve in XS NaOH

NH₃

$$[Mn(H_2O)_6]^{2+}(aq) \;+\; 2NH_3(aq) \;\longrightarrow\; [Mn(OH)_2(H_2O)_4](s) \;+\; 2NH_4^+(aq)$$

off-white pt. **insoluble in XS NH₃**

CO₃²⁻

$$[Mn(H_2O)_6]^{2+}(aq) \;+\; CO_3^{2-}(aq) \;\longrightarrow\; MnCO_3(s) \;+\; 6H_2O(l)$$

off-white pt. which darkens on standing

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

The above reactions show...   the **stability of Mn(II) in acidic** conditions
the **instability of Mn(II) in alkaline** conditions

Mn (IV)   **MnO₂(s)**   **black, insoluble solid**
catalysises the decomposition of hydrogen peroxide, H_2O_2

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.

acidic $MnO_4^-{}_{(aq)} \;+\; 8H^+{}_{(aq)} \;+\; 5e^- \;\longrightarrow\; Mn^{2+}{}_{(aq)} \;+\; 4H_2O_{(l)}$ E° = + 1.52 V

alkaline $MnO_4^-{}_{(aq)} \;+\; 2H_2O_{(l)} \;+\; 3e^- \;\longrightarrow\; MnO_{2(s)} \;+\; 4OH^-{}_{(aq)}$ E° = + 0.59 V

N.B.   Acidify with dilute H₂SO₄   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 is the first sign of a permanent pale pink colour when no more manganate(VII) reacts.

CHROMIUM

Chromium(III)   Chromium(III) ions are typical of M^{3+} ions in this block
Aqueous solutions contain violet, octahedral hexaaquachromium(III) ions
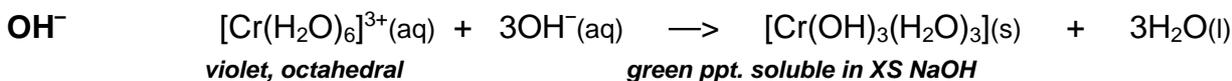
OH⁻ $[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \longrightarrow [Cr(OH)_3(H_2O)_3](s) + 3H_2O(l)$
violet, octahedral   *green ppt. soluble in XS NaOH*

As with all hydroxides the precipitate reacts with acid

$[Cr(OH)_3(H_2O)_3](s) + 3H^+(aq) \longrightarrow [Cr(H_2O)_6]^{3+}(aq)$
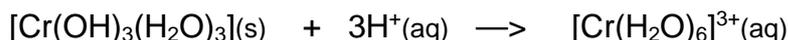
being a 3+ hydroxide it is AMPHOTERIC as it dissolves in excess alkali
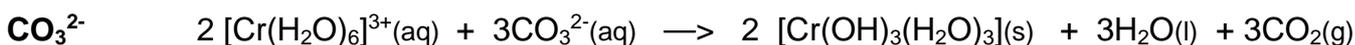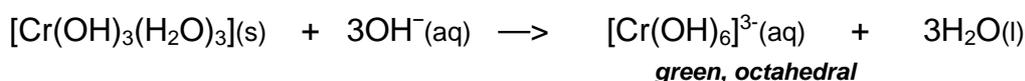
$[Cr(OH)_3(H_2O)_3](s) + 3OH^-(aq) \longrightarrow [Cr(OH)_6]^{3-}(aq) + 3H_2O(l)$
green, octahedral

CO₃²⁻ $2[Cr(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \longrightarrow 2[Cr(OH)_3(H_2O)_3](s) + 3H_2O(l) + 3CO_2(g)$

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.

NH₃ $[Cr(H_2O)_6]^{3+}(aq) + 3NH_3(aq) \longrightarrow [Cr(OH)_3(H_2O)_3](s) + 3NH_4^+(aq)$
green ppt. soluble in XS NH₃

$[Cr(OH)_3(H_2O)_3](s) + 6NH_3(aq) \longrightarrow [Cr(NH_3)_6]^{3+}(aq) + 3H_2O(l) + 3OH^-(aq)$
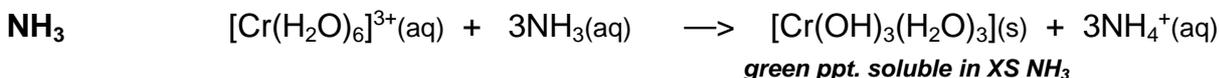
Oxidation   In the presence of alkali, Cr(III) is unstable and can be **oxidised** to Cr(VI) with peroxide.

$2Cr^{3+}(aq) + 3H_2O_2(l) + 10OH^-(aq) \longrightarrow 2CrO_4^{2-}(aq) + 8H_2O(l)$
green   *yellow*
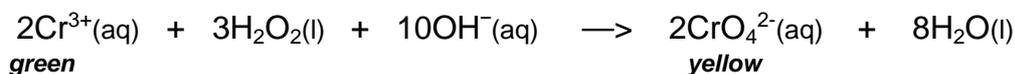
Acidification of the yellow chromate will produce the orange dichromate(VI) ion

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

$2[Cr(H_2O)_6]^{3+}(aq) + Zn(s) \longrightarrow 2[Cr(H_2O)_6]^{2+}(aq) + Zn^{2+}(aq)$
green   *blue*

Chromium (VI)	Occurs as	dichromate (VI) $Cr_2O_7^{2-}$	*orange*
	and	chromate (VI) CrO_4^{2-}	*yellow*

Interconversion **dichromate is stable in acid** solution
chromate is stable in alkaline solution.

in alkali $\mathbf{Cr_2O_7^{2-}(aq) + 2OH^-(aq) \rightleftharpoons 2CrO_4^{2-}(aq) + H_2O(l)}$

in acid $\mathbf{2\,CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)}$

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.

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) \quad [\,E° = +1.33\ V\,]$$
orange   *green*

- Its E° value is lower than Cl_2 (1.36V) so can be used in the presence of Cl^- ions
- MnO_4^- (E° = 1.52V) 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

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.

Silver (I)

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

e.g. $AgCl_{(s)}$ + $2NH_{3(aq)}$ —> $[Ag(NH_3)_2]^+_{(aq)}$ + $Cl^-_{(aq)}$
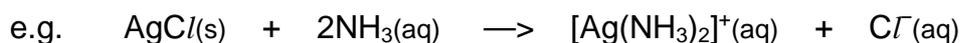
see notes on identification of halide ions in solution

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

$[Ag(NH_3)_2]^+$ • 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

$[Ag(SO_3)_2]^{3-}$ 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.

$AgBr$ + $2S_2O_3^{2-}$ —> $[Ag(S_2O_3)_2]^{3-}$ + Br^-
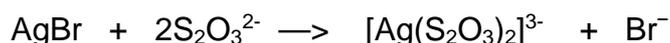
$[Ag(CN)_2]^-$ Formed when silver salts are dissolved in sodium or potassium cyanide and the solution used for silver electroplating.

Knockhardy Publishing

AQA

VANADIUM

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

$$\mathbf{E}^\circ$$

Vanadium(V)	$VO_2^+_{(aq)} + 2H^+_{(aq)} + e^- \longrightarrow VO^{2+}_{(aq)} + H_2O_{(l)}$	**+1.00 V**
	yellow ***blue***	

Vanadium(IV)	$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^- \longrightarrow V^{3+}_{(aq)} + H_2O_{(l)}$	**+0.34 V**
	blue ***blue/green***	

Vanadium(III)	$V^{3+}_{(aq)} + e^- \longrightarrow V^{2+}_{(aq)}$	**-0.26 V**
	blue/green ***lavender***	

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 neutral or negatively charged species
- conditions - addition of **sodium hydroxide** followed by **hydrogen peroxide**

e.g.

$$Fe(OH)_{2(s)} + OH^-_{(aq)} \longrightarrow Fe(OH)_{3(s)} + e^-$$

$$Co(OH)_{2(s)} + OH^-_{(aq)} \longrightarrow Co(OH)_{3(s)} + e^-$$

$$2Cr^{3+}_{(aq)} + 3H_2O_{2(l)} + 10OH^-_{(aq)} \longrightarrow 2CrO_4^{2-}_{(aq)} + 8H_2O_{(l)}$$
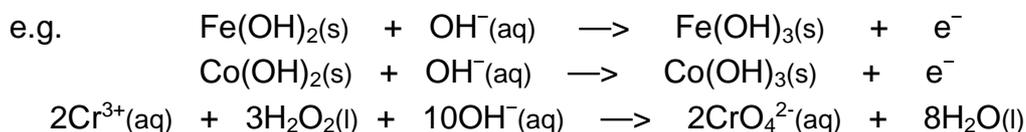
Mn(II) is also oxidised in alkaline conditions

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

$$[Co(NH_3)_6]^{2+}_{(aq)} \longrightarrow [Co(NH_3)_6]^{3+}_{(aq)} + e^-$$

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

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
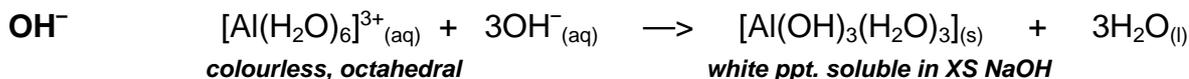
OH⁻

$$[Al(H_2O)_6]^{3+}_{(aq)} + 3OH^-_{(aq)} \longrightarrow [Al(OH)_3(H_2O)_3]_{(s)} + 3H_2O_{(l)}$$
colourless, octahedral   *white ppt. soluble in XS NaOH*

As with all hydroxides the precipitate reacts with acid

$$[Al(OH)_3(H_2O)_3]_{(s)} + 3H^+_{(aq)} \longrightarrow [Al(H_2O)_6]^{3+}_{(aq)}$$
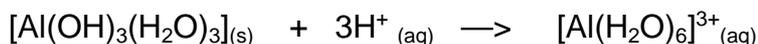
being a 3+ hydroxide it is AMPHOTERIC and dissolves in excess alkali

$$[Al(OH)_3(H_2O)_3]_{(s)} + 3OH^-_{(aq)} \longrightarrow [Al(OH)_6]^{3-}_{(aq)} + 3H_2O_{(l)}$$
colourless, octahedral

CO₃²⁻

$$2\,[Al(H_2O)_6]^{3+}_{(aq)} + 3CO_3^{2-}_{(aq)} \longrightarrow 2\,[Al(OH)_3(H_2O)_3]_{(s)} + 3H_2O_{(l)} + 3CO_{2(g)}$$

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.

NH₃

$$[Al(H_2O)_6]^{3+}_{(aq)} + 3NH_{3(aq)} \longrightarrow [Al(OH)_3(H_2O)_3]_{(s)} + 3NH_4^+_{(aq)}$$
white ppt. insoluble in XS NH₃