5.3.2 Qualitative analysis

Testing for Negative ions (anions)

Testing for presence of a carbonate

Add any dilute acid and observe effervescence.
Bubble gas through limewater to test for CO_2 – will turn limewater cloudy

$2HCl + Na_2CO_3 \rightarrow 2NaCl + H_2O + CO_2$

Fizzing due to CO_2 would be observed if a carbonate was present

Testing for presence of a sulfate

Acidified $BaCl_2$ solution is used as a reagent to test for sulfate ions

If **barium chloride** is added to a solution that contains sulphate ions a **white precipitate** forms

$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$.

Other anions should give a negative result which is no precipitate forming

The acid is needed to react with carbonate impurities that are often found in salts which would form a white barium carbonate precipitate and so give a false result

Sulfuric acid cannot be used to acidify the mixture because it contains sulphate ions which would form a precipitate

Testing for halide ions with silver nitrate.

This reaction is used as a test to identify which halide ion is present. The test solution is made acidic with **nitric acid,** and then **silver nitrate solution** is added dropwise.

The role of nitric acid is to react with any carbonates present to prevent formation of the precipitate Ag_2CO_3. This would mask the desired observations

$2HNO_3 + Na_2CO_3 \rightarrow 2NaNO_3 + H_2O + CO_2$

Fluorides produce no precipitate
Chlorides produce a **white** precipitate
$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
Bromides produce a **cream** precipitate
$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
Iodides produce a **pale yellow** precipitate
$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$

Hydrochloric acid cannot be used to acidify the mixture because it contains chloride ions which would form a precipitate

The silver halide precipitates can be treated with ammonia solution to help differentiate between them if the colours look similar:

Silver chloride dissolves in **dilute ammonia** to form a complex ion
$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$
Colourless solution
Silver bromide dissolves in **concentrated ammonia** to form a complex ion
$AgBr(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Br^-(aq)$
Colourless solution
Silver iodide does not react with ammonia – it is too insoluble.

The sequence of tests required is carbonate, sulfate then halide. (This will prevent false results of as both $BaCO_3$ and Ag_2SO_4 are insoluble.)

Testing for positive ions (cations)

Test for ammonium ion NH_4^+, by reacting with warm NaOH(aq) forming NH_3 gas

Ammonia gas can be identified by its pungent smell or by turning red litmus paper blue

Precipitation Reactions with sodium hydroxide and ammonia

The bases OH^- and ammonia when in limited amounts form the same hydroxide precipitates.

These reactions are classed as precipitation reactions

$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Cu(H_2O)_4(OH)_2{}_{(s)} + 2H_2O{}_{(l)}$

Blue solution — blue ppt

$Cu^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Cu(OH)_2{}_{(s)}$

Blue solution — blue ppt

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

Very pale pink solution — Pale brown ppt

$Mn^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Mn(OH)_2{}_{(s)}$

Very pale pink solution — Pale brown ppt

$[Fe(H_2O)_6]^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Fe(H_2O)_4(OH)_2{}_{(s)} + 2H_2O{}_{(l)}$

green solution — green ppt

$Fe^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Fe(OH)_2{}_{(s)}$

green solution — green ppt

$[Fe(H_2O)_6]^{3+}{}_{(aq)} + 3OH^-{}_{(aq)} \rightarrow Fe(H_2O)_3(OH)_3{}_{(s)} + 3H_2O{}_{(l)}$

Yellow/brown solution — brown ppt

$Fe^{3+}{}_{(aq)} + 3OH^-{}_{(aq)} \rightarrow Fe(OH)_3{}_{(s)}$

Yellow/brown solution — brown ppt

$[Cr(H_2O)_6]^{3+}{}_{(aq)} + 3OH^-{}_{(aq)} \rightarrow Cr(H_2O)_3(OH)_3{}_{(s)} + 3H_2O{}_{(l)}$

green solution — green ppt

$Cr^{3+}{}_{(aq)} + 3OH^-{}_{(aq)} \rightarrow Cr(OH)_3{}_{(s)}$

green solution — green ppt

With ammonia when added in limited amounts the same hydroxide precipitates form. The ammonia acts as a base, removes a proton from the aqueous complex and becomes the ammonium ion

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

$$[Fe(H_2O)_6]^{3+}{}_{(aq)} + 3NH_3{}_{(aq)} \rightarrow Fe(H_2O)_3(OH)_3{}_{(s)} + 3NH_4^+{}_{(aq)}$$

Reaction with excess OH^-

With excess NaOH, the Cr hydroxide dissolves.
Cr becomes $[Cr(OH)_6]^{3-}$ (aq) green solution

•This hydroxide is classed as **amphoteric** because it can react with alkali to give a solution and react with acid to form the aqueous salt

$Cr(H_2O)_3(OH)_3{}_{(s)} + 3OH^-{}_{(aq)} \rightarrow [Cr(OH)_6]^{3-}{}_{(aq)} + 3H_2O_{(l)}$

$Cr(H_2O)_3(OH)_3{}_{(s)} + 3H^+{}_{(aq)} \rightarrow [Cr(H_2O)_6]^{3+}{}_{(aq)}$

Reaction with excess NH_3

With **excess NH_3 ligand exchange** reactions occur with Cu and Cr, and their hydroxide precipitates dissolve in excess ammonia

The ligands NH_3 and H_2O are similar in size and are uncharged. Ligand exchange occurs without change of co-ordination number for Cr

Cr becomes $[Cr(NH_3)_6]^{3+}$ purple solution

This substitution may, however, be incomplete as in the case with Cu

Cu becomes $[Cu(NH_3)_4(H_2O)_2]^{2+}$ deep blue solution

$$Cr(OH)_3(H_2O)_{3(s)} + 6NH_3{}_{(aq)} \rightarrow [Cr(NH_3)_6]^{3+}{}_{(aq)} + 3H_2O_{(l)} + 3OH^-{}_{(aq)}$$

$$Cu(OH)_2(H_2O)_{4(s)} + 4NH_3{}_{(aq)} \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}{}_{(aq)} + 2H_2O{}_{(l)} + 2OH^-{}_{(aq)}$$