Qualitative Analysis — The testing → of a substance or mixture to determine its chemical constituents

Group I → Ag^+ — **In presence of dilute HCl** → Insoluble **White precipitate** of AgCl

$$Ag^+_{(aq)} + Cl^-_{(aq)} \longrightarrow AgCl_{(s)} \text{ (White ppt.)}$$

$Pb_2{}^+$ — In presence of

Dil. HCl or other soluble chlorides → **precipitate white** lead(II) chloride from moderately concentrated solutions of lead(II) salts

$$Pb^{2+}(aq) + 2Cl^-(aq) \longrightarrow PbCl_2(s)$$

The precipitate **dissolves** in an **excess** of **concentrated hydrochloric acid** to give yellow solutions containing various species including $PbCl_3^-$ and $PbCl_4^{2-}$.

NaOH solution — gives a → **white precipitate** of lead(II) hydroxide which is soluble in excess NaOH to give colourless sodium plumbate(II)

$$Pb^{2+}(aq) + 2OH^-(aq) \longrightarrow Pb(OH)_2(s) \Rightarrow Pb(OH)_2(s) + 2OH^-(aq) \longrightarrow [Pb(OH)_4]^{2-}(aq)$$

Potassium iodide solution — gives a → **bright yellow** precipitate of lead(II) iodide. This will dissolve in boiling water to give a colourless solution - the colour comes from interactions in the crystal lattice rather than from coloured ions

$$Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$$

Potassium chromate(VI) solution — gives a → **bright yellow** precipitate of lead(II) chromate(VI)

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow PbCrO_4(s)$$

Group II — We will study → Hg_2^{2+}, Cu^{2+}, Bi^{3+}

Hg_2^{2+} — **Addition of HCl** → $Hg_2^{2+}(aq) + 2\,Cl^-(aq) \longrightarrow Hg_2Cl_2(s)$

Now add ammonia and water

Ammonia also reacts with Hg2Cl2 via a rather unusual oxidation-reduction reaction. The products include finely divided metallic Hg, which is black, and a compound of formula $HgNH_2Cl$, which is white.

$$\underset{\text{white}}{Hg_2Cl_2(s)} + 2\,NH_3(aq) \longrightarrow \underset{\text{black}}{Hg(l)} + \underset{\text{white}}{HgNH_2Cl(s)} + NH_4^+(aq) + Cl^-(aq)$$

Cu^{2+}

With water and in presence of

NaOH solution — gives a → pale blue precipitate usually described as copper(II) hydroxide

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

In fact this precipitate is the basic salt – thus from copper(II) sulphate solution the product is basic copper

$$2[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) + SO_4^{2-}(aq) \longrightarrow Cu(OH)_2.CuSO_4(s) + 12H_2O(l)$$

Ammonia solution — Initially → gives a **blue precipitate** as for sodium hydroxide

Further Addition of **NH_3**

gives **deep blue** soluble **cuprammine complexes** whose composition depends on the amount of ammonia present. The reaction is usually represented

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

Conc. HCl — gives a → **bright green solution** containing $CuCl_4^{2-}$ ions; dilution with water causes the solution to turn pale blue as the $[Cu(H_2O)_6]^{2+}$ ion re-forms

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

Bi^{3+}

In presence of NH_3(aq) and water

$Bi^{3+}(aq) + 2NH_3(aq) + 3H_2O \longrightarrow BI(OH)_3(s) + 3NH_4^+(aq)$

Now

The $Bi(OH)_3$ that remains is now dissolved and confirmed with the addition of **freshly prepared sodium stannite**, $Na_2Sn(OH)_4$ to a basic solution. The Bi^{3+} ion is reduced to **black bismuth** metal, confirming its presence in solution.

$Bi(OH)_3(s) + 3/2\ Sn(OH)_4^{2-}(aq) \longrightarrow Bi(s) + 3/2Sn(OH)_6^{2-}$

Another test can be perform as

Bismuth is detected by the orange coloured precipitate that is formed when hydrogen sulphide is passed into an acidified solution of the substance under test.

Group III

Here We will study

Fe^{3+}, Cr^{3+}, Al^{3+}, Zn^{2+}, Mn^{2+}

Fe^{3+}

With H_2O and in presence of

NaOH solution

precipitates

foxy-red iron(III) hydroxide, insoluble in excess alkali

$[Fe(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s) + 6H_2O(l)$

Potassium hexacyanoferrate(II)

precipitates

dark blue potassium iron(III) hexacyanoferrate(II), Prussian Blue

$K^+(aq) + Fe^{3+}(aq) + [Fe(CN)_6]^{4-}(aq) \longrightarrow KFe^{3+}[Fe^{2+}(CN)_6](s)$

Al^{3+}

With H_2O and in presence of

NaOH solution

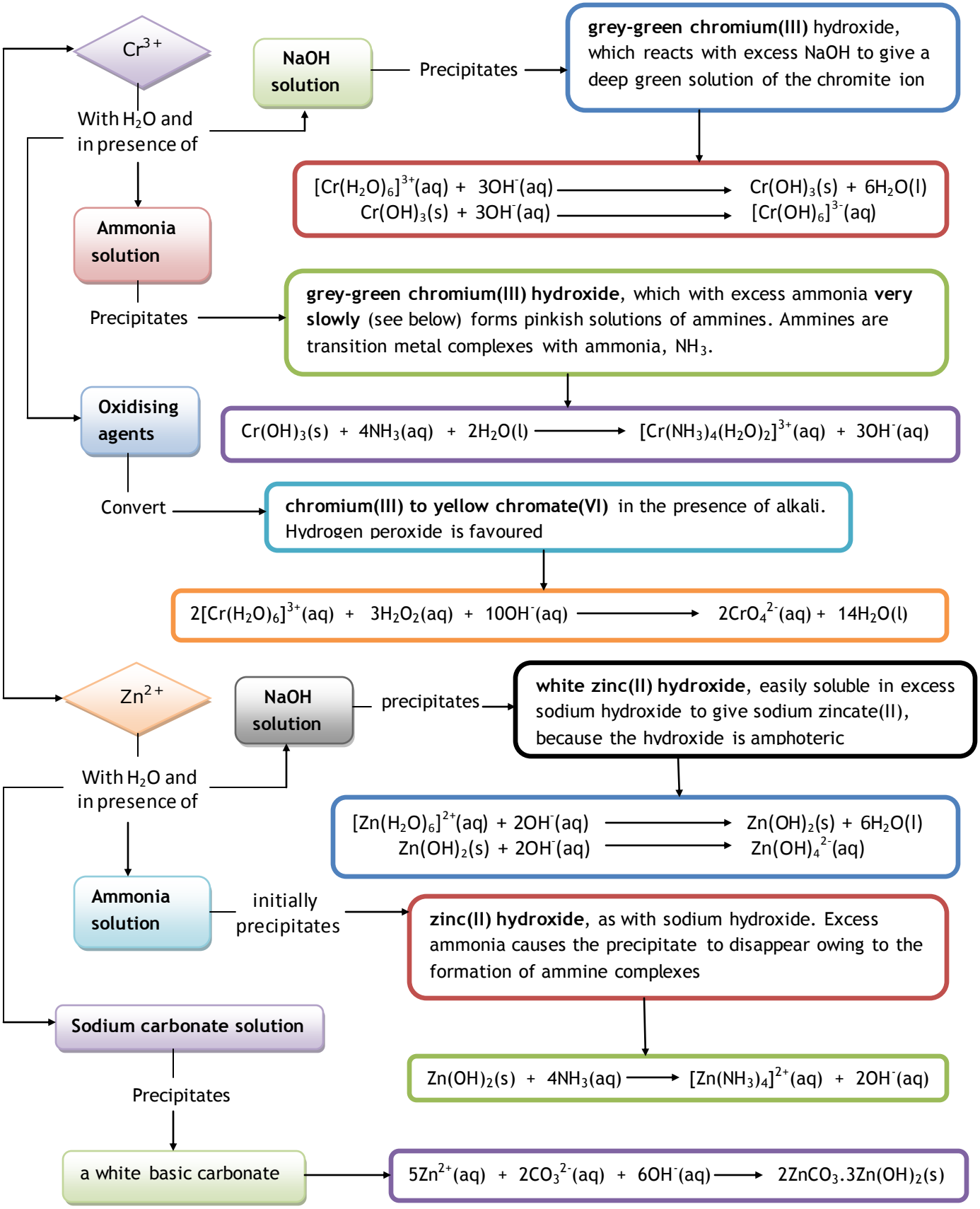
precipitates

white gelatinous aluminium hydroxide. This reacts with excess NaOH to give a colourless solution of sodium aluminate

$[Al(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \longrightarrow Al(OH)_3(s) + 6H_2O(l)$

$Al(OH)_3(s) + 3OH^-(aq) \longrightarrow [Al(OH)_6]^{3-}(aq)$

Ammonia solution precipitates white aluminium hydroxide, as with NaOH; however it does not react further with excess ammonia


Cr^{3+}
With H_2O and in presence of
NaOH solution
Precipitates
grey-green chromium(III) hydroxide, which reacts with excess NaOH to give a deep green solution of the chromite ion
$[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \longrightarrow Cr(OH)_3(s) + 6H_2O(l)$
$Cr(OH)_3(s) + 3OH^-(aq) \longrightarrow [Cr(OH)_6]^{3-}(aq)$
Ammonia solution
Precipitates
grey-green chromium(III) hydroxide, which with excess ammonia very slowly (see below) forms pinkish solutions of ammines. Ammines are transition metal complexes with ammonia, NH_3.
$Cr(OH)_3(s) + 4NH_3(aq) + 2H_2O(l) \longrightarrow [Cr(NH_3)_4(H_2O)_2]^{3+}(aq) + 3OH^-(aq)$
Oxidising agents
Convert
chromium(III) to yellow chromate(VI) in the presence of alkali. Hydrogen peroxide is favoured
$2[Cr(H_2O)_6]^{3+}(aq) + 3H_2O_2(aq) + 10OH^-(aq) \longrightarrow 2CrO_4^{2-}(aq) + 14H_2O(l)$
Zn^{2+}
With H_2O and in presence of
NaOH solution
precipitates
white zinc(II) hydroxide, easily soluble in excess sodium hydroxide to give sodium zincate(II), because the hydroxide is amphoteric
$[Zn(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s) + 6H_2O(l)$
$Zn(OH)_2(s) + 2OH^-(aq) \longrightarrow Zn(OH)_4^{2-}(aq)$
Ammonia solution
initially precipitates
zinc(II) hydroxide, as with sodium hydroxide. Excess ammonia causes the precipitate to disappear owing to the formation of ammine complexes
$Zn(OH)_2(s) + 4NH_3(aq) \longrightarrow [Zn(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$
Sodium carbonate solution
Precipitates
a white basic carbonate
$5Zn^{2+}(aq) + 2CO_3^{2-}(aq) + 6OH^-(aq) \longrightarrow 2ZnCO_3.3Zn(OH)_2(s)$

Mn^{2+}

With H_2O and in presence of

NaOH solution — Precipitates → **beige manganese(II) hydroxide.** This is insoluble in excess reagent, and rapidly darkens owing to oxidation to hydrated

$$[Mn(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \longrightarrow Mn(OH)_2(s) + 6H_2O(l)$$
$$4Mn(OH)_2(s) + 2H_2O(l) + O_2(aq) \longrightarrow 4MnO_2.H_2O(s)$$

Sodium or potassium carbonate solution — Gives → **a white precipitate** of manganese(II) carbonate

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

Lead(IV) oxide

in the presence of → **nitric acid converts** manganese(II) into purple manganate(VII); an alternative oxidising agent is sodium bismuthate(V), $NaBiO_3$

$$5PbO_2(s) + 2Mn^{2+}(aq) + 6H^+(aq) \downarrow \longrightarrow 2MnO_4^-(aq) + 5Pb^{2+}(aq) + 2H_2O(l)$$
$$5BiO_3^-(aq) + 14H^+(aq) + 2Mn^{2+}(aq) \longrightarrow 5Bi^{3+}(aq) + 2MnO_4^-(aq) + 7H_2O(l)$$

A small amount of lead(IV) oxide or of sodium bismuthate(V) is added to the test solution, 6 or so drops of concentrated nitric acid added, and the mixture boiled. Filtration will give a purple filtrate if Mn^{2+} was present

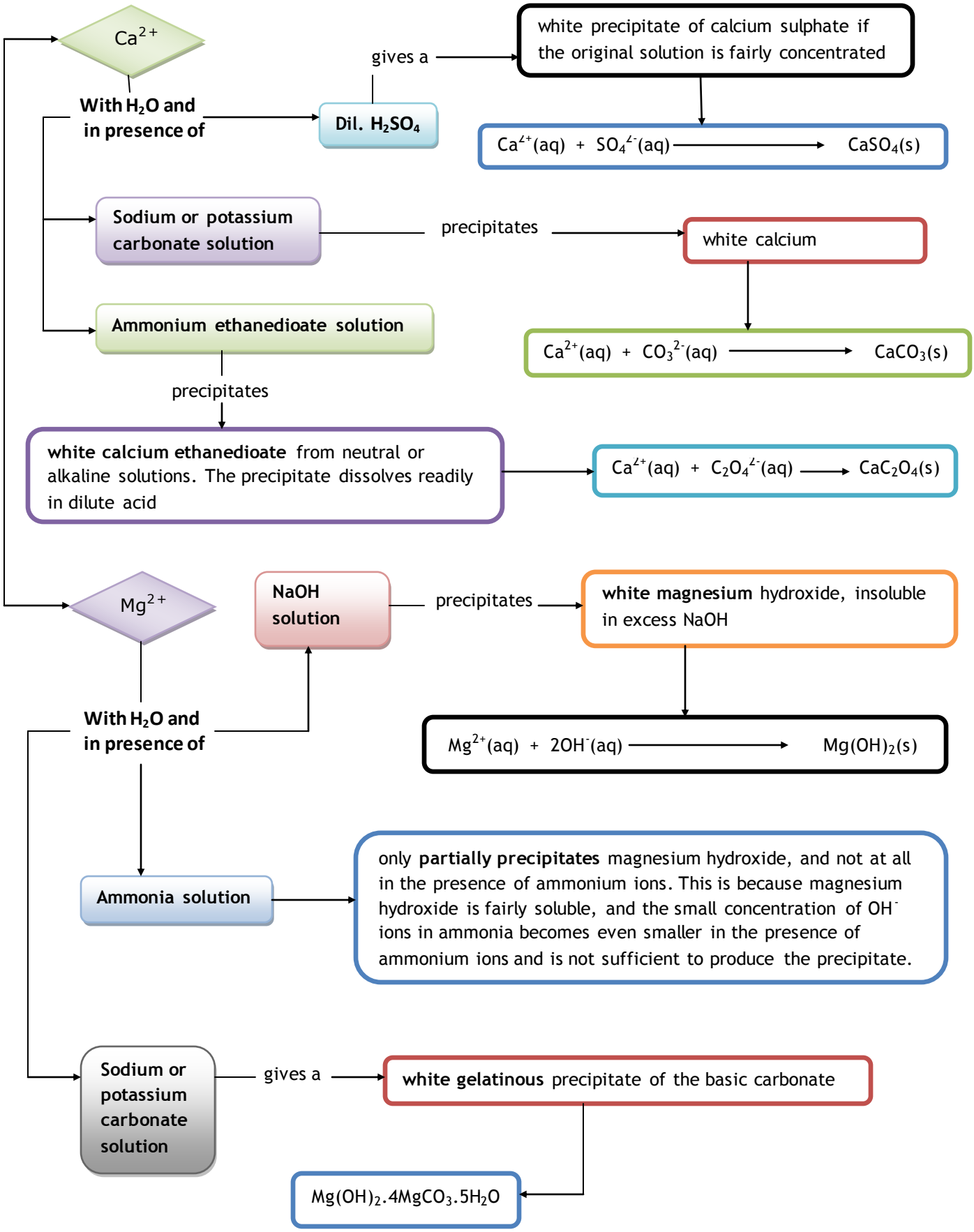
Group IV — Here We will study → Ca^{2+}, Ba^{2+}, Mg^{2+}

Ba^{2+} — With **H_2SO_4** → A white precipitate will form → $Ba^{2+} + SO_4^{2-} \rightarrow$

Flame — In the presence → High Conc. of CrO_4^{2-} → **The yellow precipitate** produced by the barium test confirms the presence of barium. The reaction occurs as follows

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow$$

On Burning Light green (slight) color


Ca^{2+}
With H_2O and in presence of
Dil. H_2SO_4
gives a
white precipitate of calcium sulphate if the original solution is fairly concentrated
$Ca^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow CaSO_4(s)$
Sodium or potassium carbonate solution
precipitates
white calcium
$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$
Ammonium ethanedioate solution
precipitates
white calcium ethanedioate from neutral or alkaline solutions. The precipitate dissolves readily in dilute acid
$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \longrightarrow CaC_2O_4(s)$
Mg^{2+}
NaOH solution
precipitates
white magnesium hydroxide, insoluble in excess NaOH
$Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s)$
With H_2O and in presence of
Ammonia solution
only partially precipitates magnesium hydroxide, and not at all in the presence of ammonium ions. This is because magnesium hydroxide is fairly soluble, and the small concentration of OH^- ions in ammonia becomes even smaller in the presence of ammonium ions and is not sufficient to produce the precipitate.
Sodium or potassium carbonate solution
gives a
white gelatinous precipitate of the basic carbonate
$Mg(OH)_2.4MgCO_3.5H_2O$

Halides — Here we will study about → Cl^- , Br^- , I^-

Cl^-

with → **Conc. H_2SO_4** — liberates → steamy acidic fumes of HCl from solid chlorides

$NaCl(s) + H_2SO_4(l) \longrightarrow NaHSO_4(s) +$

with → **Silver nitrate solution**

added to a solution of a chloride that has been acidified (test with blue litmus paper) with dilute nitric acid gives a white precipitate of silver chloride. The precipitate is readily soluble in dilute ammonia or in sodium thiosulphate solution

$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

$AgCl(s) + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$

$AgCl(s) + 2S_2O_3^{2-}(aq) \longrightarrow [Ag(S_2O_3)_2]^{3-}(aq) + Cl^-$

Dil.HCl

Any soluble silver salt + any soluble chloride gives a white silver chloride precipitate, that darkens in light.

$Ag^+_{(aq)} + Cl^-_{(aq)} \longrightarrow AgCl_{(s)}$

$Pb^{2+}_{(aq)} + 2Cl^-_{(aq)} \longrightarrow PbCl_{2(s)}$

Br^-

with → **Conc. H_2SO_4** — gives a → mixture of hydrogen bromide, bromine and sulphur dioxide with solid bromides; the HBr produced is oxidised by sulphuric acid. The mixture evolves steamy brownish acidic fumes

$NaBr(s) + H_2SO_4(l) \longrightarrow NaHSO_4(s) + HBr(g)$

$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$

Silver nitrate solution

added to a solution of a bromide that has been acidified (test with blue litmus paper) with dilute nitric acid gives a cream precipitate of silver bromide. The precipitate is readily soluble in *concentrated* ammonia

$Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$

$AgBr(s) + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]^+(aq) + Br^-(aq)$

I^-

with

Conc. H_2SO_4 — gives a → mixture of hydrogen iodide, iodine, hydrogen sulphide, sulphur and sulphur dioxide when added to solid iodides; the HI produced is oxidised by sulphuric acid. The mixture evolves purple acidic fumes, turns to a brown slurry, and is a mess

$$NaI(s) + H_2SO_4(l) \longrightarrow NaHSO_4(s) + HI(g)$$
$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$
$$6HI + H_2SO_4 \longrightarrow 3I_2 + S + 4H_2O$$
$$8HI + H_2SO_4 \longrightarrow 4I_2 + H_2S + 4H_2O$$

Silver nitrate → added to a solution of an iodide that has been acidified (test with blue litmus paper) with dilute nitric acid gives a yellow precipitate of silver iodide. The precipitate is insoluble even in concentrated ammonia

$$Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$$

Solutions of copper(II) salts — give a → brown mixture containing iodine and copper(I) iodide when added to solutions of iodides. Addition of sodium thiosulphate solution decolourises the iodine and leaves pinkish-cream copper(I) iodide as a precipitate

$$2Cu^{2+}(aq) + 4I\text{-}(aq) \longrightarrow 2CuI(s) + I_2(aq) \Rightarrow 2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Nitrate → Since all nitrates are water soluble, there is no precipitation reaction for this ion

Solid nitrates decompose on

- those of group 1 → (except Li) give the nitrite and oxygen

$$2NaNO_3(s) \longrightarrow 2NaNO_2(s) + O_2(g)$$

- All others give → the metal oxide, nitrogen dioxide, and oxygen. A brown gas is emitted that re-lights a glowing splint

$$2Pb(NO_3)_2(s) \longrightarrow 2PbO(s) + O_2(g) + 2NO_2(g)$$

Nitrate ions are reduced → The aluminium powder is a powerful reducing agent and converts the nitrate ion, **NO_3^-**, into ammonia gas, **NH_3**

$$3NO_3^-(aq) + 8Al(s) + 18H_2O(l) + 21\ OH^-(aq) \longrightarrow 8[Al(OH)_6]^{3-}(aq) + 3NH_3(g)$$

Sulphate SO_4^{2-}

$BaSO_4$, $SrSO_4$ and $PbSO_4$ are insoluble; $CaSO_4$ is sparingly soluble.

Barium chloride solution added to the test solution acidified with dilute hydrochloric acid gives a white precipitate of barium sulphate

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

addition of HCl — destroys → any carbonate or sulphite ions present so prevents the spurious positive result due to the precipitation of these barium salts. Barium nitrate solution can be used instead of barium chloride

Lead ethanoate solution — gives a → precipitate of white lead sulphate

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$$

Sulphide ion S^{2-}

if

soluble

Add

a few drops lead(II) ethanoate solution

Black ppt. of lead sulphide

$$Pb^{2+}_{(aq)} + S^{2-}_{(aq)} \longrightarrow PbS_{(s)}$$

solid

Add

dil. HCl(aq) acid, test smelly gas with damp lead(II) ethanoate paper (old name *lead acetate*)

Rotten egg smell of hydrogen sulphide and the H_2S gas turns lead(II) ethanoate paper black.

$$MS_{(s)} + 2H^+_{(aq)} \longrightarrow M^{2+}_{(aq)} + H_2S_{(g)}$$

(e.g. M = Pb, Fe, Cu, Ni etc.)