

Chemistry of some Transition elements: V, Mn, Co, Cu, Cr and Ag

Vanadium

Vanadium has four main oxidation states. Each one has a different colour.

VO_2^+ O.N. 5 yellow solution

VO^{2+} O.N. 4 blue solution

V^{3+} O.N. 3 green solution

V^{2+} O.N. 2 mauve solution



The ion with Vanadium in its oxidation state of 5 exists as a solid compound in the form of a VO_3^- ion, usually as NH_4VO_3 (ammonium vanadate (V)).

It is a reasonably strong oxidising agent. Addition of acid to the solid will turn into the yellow solution containing the VO_2^+ ion.

Oxidation State	Ion	Colour	Redox Equation	E° Values
+5	VO_3^- or VO_2^+	YELLOW	$\text{VO}_2^+(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}$	+1.00 V
+4	VO^{2+}	BLUE	$\text{VO}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}$	+0.34 V
+3	V^{3+}	GREEN	$\text{V}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{V}^{2+}(\text{aq})$	- 0.26 V
+2	V^{2+}	VIOLET		

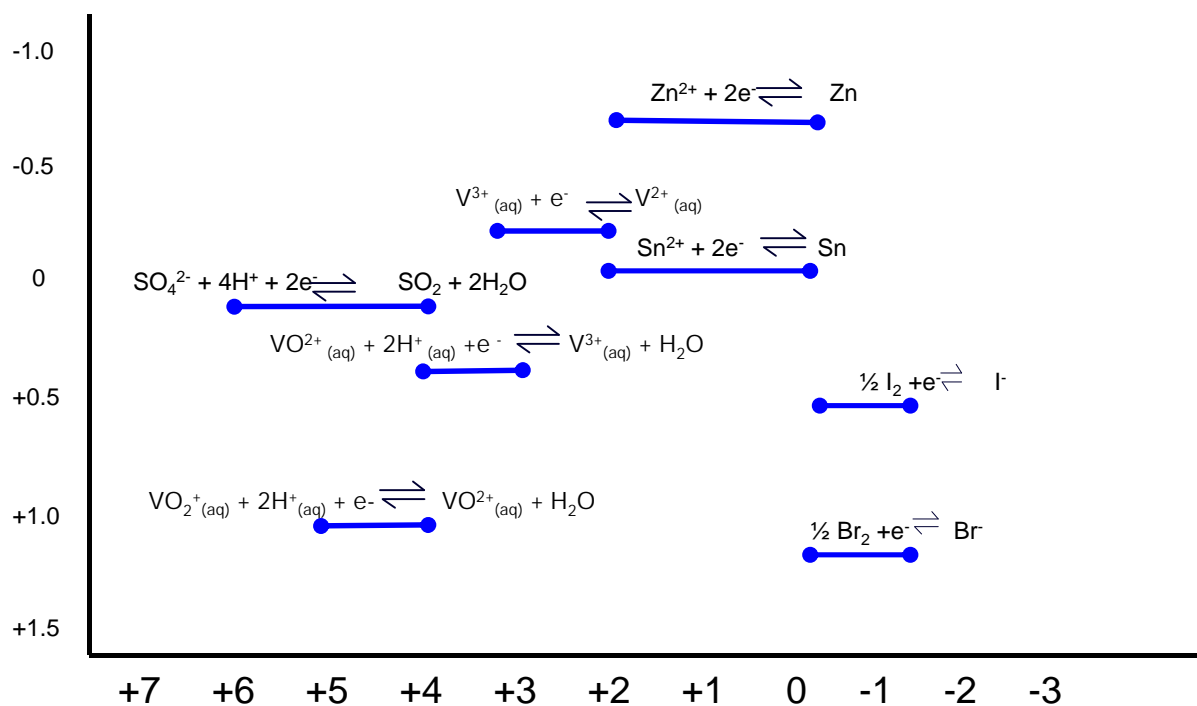
The most stable ion is the V^{3+} .

The V^{2+} ion is relatively unstable and will oxidise on standing in air to produce V^{3+} (similar to iron)

Addition of the reducing agent zinc metal to the vanadium (V) will reduce the vanadium down through each successive oxidation state. Each colour will appear in turn.



As zinc has a more negative electrode potential than all the vanadium half equations, zinc will reduce down to V^{2+}



Tin metal will only reduce the vanadium from +5 to the +3 state

Similarly iodide ions will reduce the vanadium from +5 to the +3 state

Manganese

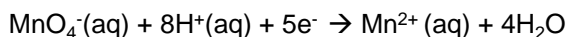
Manganese can form several oxidation states. The three main ones are:

MnO_4^- (aq) O.N. +7 purple solution

MnO_2 O.N. 4 brown solid

$\text{Mn}^{2+}/[\text{Mn}(\text{H}_2\text{O}_6)]^{2+}$ O.N. 2 very pale pink solution

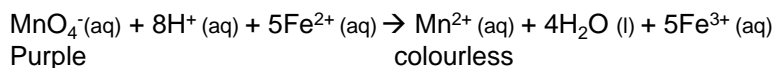
The MnO_4^- ion is a strong oxidising agent. It reduces to Mn^{2+} .



It is used to oxidise various organic substances, it can also be used in quantitative titrations.

Manganate Redox Titration

The redox titration between Fe^{2+} with MnO_4^- (purple) is a very common exercise. This titration is self-indicating because of the significant colour change from reactant to product.



The purple colour of manganate can make it difficult to see the bottom of the meniscus in the burette.

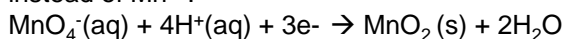
If the manganate is in the burette then the end point of the titration will be the first permanent pink colour.
Colourless \rightarrow purple

Choosing correct acid for manganate titrations.

The acid is needed to supply the 8H^+ ions. Some acids are not suitable as they set up alternative redox reactions and hence make the titration readings inaccurate.

Only **use dilute sulfuric acid** for manganate titrations.

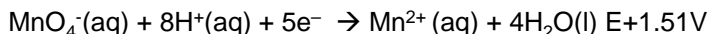
Insufficient volumes of sulfuric acid will mean the solution is not acidic enough and MnO_2 will be produced instead of Mn^{2+} .



The brown MnO_2 will mask the colour change and lead to a greater (inaccurate) volume of manganate being used in the titration.

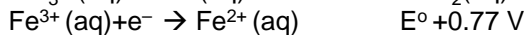
Using a weak acid like ethanoic acid would have the same effect as it cannot supply the large amount of hydrogen ions needed (8H^+).

It cannot be **conc HCl** as the Cl^- ions would be oxidised to Cl_2 by MnO_4^- as the $E^\circ \text{MnO}_4^-/\text{Mn}^{2+} > E^\circ \text{Cl}_2/\text{Cl}^-$



This would lead to a greater volume of manganate being used and poisonous Cl_2 being produced.

It cannot be nitric acid as it is an oxidising agent. It oxidises Fe^{2+} to Fe^{3+} as $E^\circ \text{NO}_3^-/\text{HNO}_2 > E^\circ \text{Fe}^{3+}/\text{Fe}^{2+}$



This would lead to a smaller volume of manganate being used.

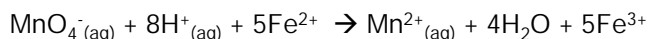
Be able to perform calculations for these titrations and for others when the reductant and its oxidation product are given.

Manganate titration example

A 2.41g nail made from an alloy containing iron is dissolved in 100cm³ acid. The solution formed contains Fe(II) ions.

10cm³ portions of this solution are titrated with potassium manganate (VII) solution of 0.02M. 9.80cm³ of KMnO₄ were needed to react with the solution containing the iron.

What is the percentage of Iron by mass in the nail?



Step1 : find moles of KMnO₄

moles = conc x vol

$$0.02 \times 9.8/1000$$

$$= 1.96 \times 10^{-4} \text{ mol}$$

Step 2 : using balanced equation find moles Fe²⁺ in 10cm³

$$= \text{moles of KMnO}_4 \times 5$$

$$= 9.8 \times 10^{-4} \text{ mol}$$

Step 3 : find moles Fe²⁺ in 100cm³

$$= 9.8 \times 10^{-4} \text{ mol} \times 10$$

$$= 9.8 \times 10^{-3} \text{ mol}$$

Step 4 : find mass of Fe in 9.8x10⁻³ mol

$$\text{mass} = \text{moles} \times \text{RAM} = 9.8 \times 10^{-3} \times 55.8 = 0.547\text{g}$$

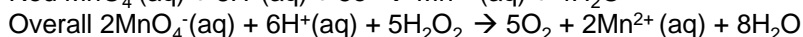
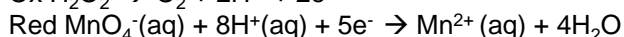
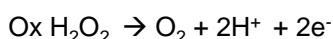
Step 5 : find % mass

$$\% \text{mass} = 0.547/2.41 \times 100$$

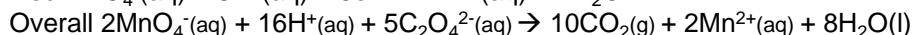
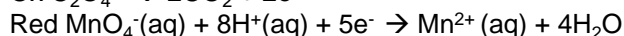
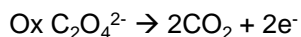
$$= 22.6\%$$

Other useful manganate titrations

With hydrogen peroxide

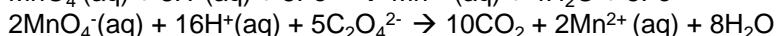
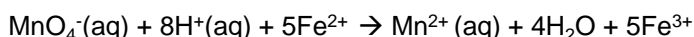


With ethanedioate

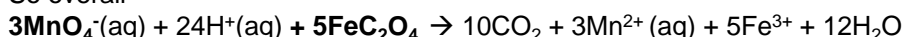


The reaction between MnO₄⁻ and C₂O₄²⁻ is slow to begin with (as the reaction is between two negative ions). To do as a titration the conical flask can be heated to 60° C to speed up the initial reaction.

With Iron (II) ethanedioate both the Fe²⁺ and the C₂O₄²⁻ react with the MnO₄⁻
1MnO₄⁻ reacts with 5Fe²⁺ and 2 MnO₄⁻ reacts with 5C₂O₄²⁻



So overall



So overall the ratio is 3 MnO₄⁻ to 5 FeC₂O₄

A 1.412 g sample of impure FeC₂O₄.2H₂O was dissolved in an excess of dilute sulphuric acid and made up to 250 cm³ of solution. 25.0 cm³ of this solution decolourised 23.45 cm³ of a 0.0189 mol dm⁻³ solution of potassium manganate(VII).

What is the percentage by mass of FeC₂O₄.2H₂O in the original sample?

Step1 : find moles of KMnO₄

moles = conc x vol

$$0.0189 \times 23.45/1000$$

$$= 4.43 \times 10^{-4} \text{ mol}$$

Step 2 : using balanced equation find moles FeC₂O₄.2H₂O in 25cm³

$$= \text{moles of KMnO}_4 \times 5/3 \text{ (see above for ratio)}$$

$$= 7.39 \times 10^{-4} \text{ mol}$$

Step 3 : find moles FeC₂O₄.2H₂O in 250 cm³

$$= 7.39 \times 10^{-4} \text{ mol} \times 10$$

$$= 7.39 \times 10^{-3} \text{ mol}$$

Step 4 : find mass of FeC₂O₄.2H₂O in 7.39x10⁻³ mol

$$\text{mass} = \text{moles} \times \text{Mr} = 7.39 \times 10^{-3} \times 179.8 = 1.33\text{g}$$

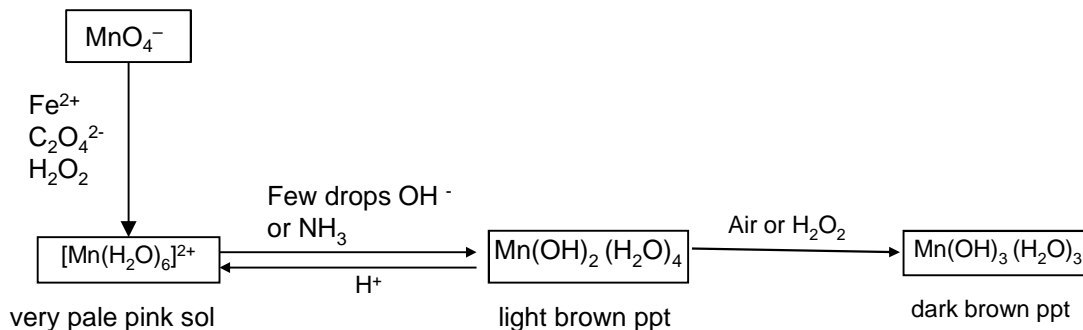
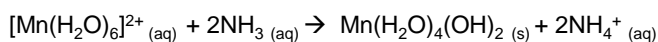
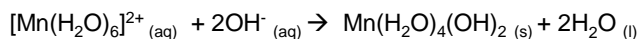
Step 5 ; find % mass

$$\% \text{mass} = 1.33/1.412 \times 100$$

$$= 94.1\%$$

Reaction of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ with limited OH^- and limited NH_3

The bases OH^- and ammonia when in limited amounts form the same manganese hydroxide precipitate. They form in deprotonation acid base reactions. This hydroxide can oxidise on standing in air to manganese (III) hydroxide.



Cobalt reactions.

Cobalt two main oxidation states are +2 and +3

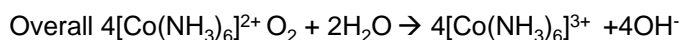
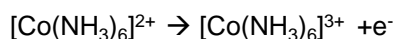
Oxidation of Cobalt

$[\text{Co}(\text{H}_2\text{O})_6]^{2+} (\text{aq}) \xrightarrow{\text{little OH}^- \text{ or NH}_3} \text{Co}(\text{H}_2\text{O})_4(\text{OH})_2 (\text{s}) \xrightarrow{\text{O}_2} \text{Co}(\text{H}_2\text{O})_3(\text{OH})_3 (\text{s})$
 pink solution \rightarrow blue precipitate \rightarrow brown precipitate

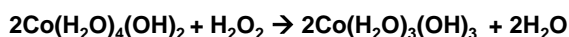
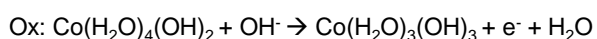
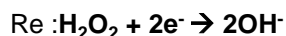
$[\text{Co}(\text{H}_2\text{O})_6]^{2+} (\text{aq}) \xrightarrow{\text{Excess NH}_3} [\text{Co}(\text{NH}_3)_6]^{2+} (\text{aq}) \xrightarrow{\text{O}_2} [\text{Co}(\text{NH}_3)_6]^{3+} (\text{aq}) + \text{e}^-$
 yellow solution \rightarrow Brown solution

Ammonia ligands make the Co(II) state unstable and easier to oxidise. Air oxidises Co(II) to Co(III).
 H_2O_2 could also bring about the oxidation

The O_2 half equation for these reactions is:- $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$

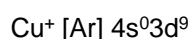


The H_2O_2 half equation for these reactions is



Copper Chemistry

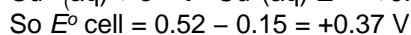
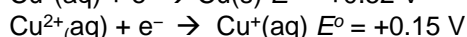
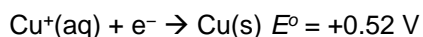
Copper has two main oxidation states in its compounds, +2 and +1. The +1 state is much less stable than the +2



Copper(I) compounds are colourless in solution. In Cu^+ ions the 3d sub shell is full e.g. $3d^{10}$. There is no space for electrons to transfer, so there is not an energy transfer equal to that of visible light.

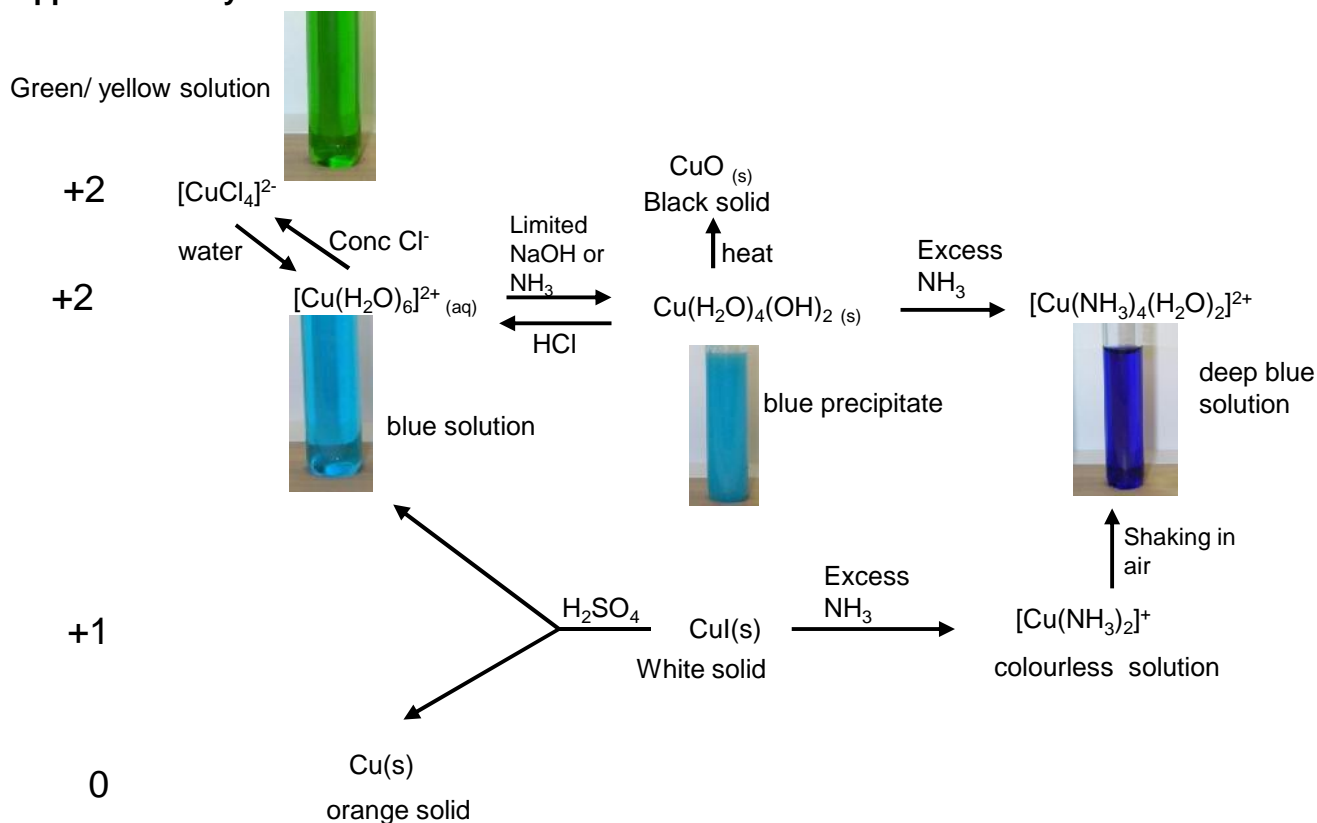
Disproportionation of copper(I) iodide

Copper(I) iodide when reacting with sulfuric acid will disproportionate to produce Cu^{2+} and Cu metal



As $E^\circ_{\text{Cu}^+/\text{Cu}} > E^\circ_{\text{Cu}^{2+}/\text{Cu}^+}$ and E_{cell} has a positive value of +0.37V, Cu^+ disproportionates from +1 oxidation state to 0 in Cu and +2 in Cu^{2+}

Copper Summary

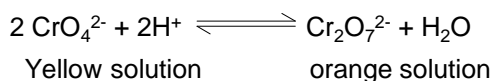


Chromium Chemistry

Chromium has three main oxidation states in its compounds, +6, +3 and +2. The +2 state is much less stable than the +3. When in the +6 state chromium compounds can be strong oxidising agents.

Chromate/ dichromate equilibrium

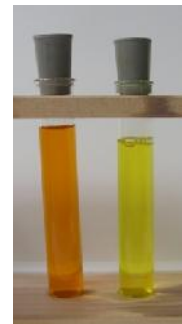
The chromate CrO_4^{2-} and dichromate $\text{Cr}_2\text{O}_7^{2-}$ ions both have oxidation states of +6. They can be converted from one to the other by the following equilibrium reaction.



Addition of acid will by application of le Chatelier push the equilibrium to the dichromate.

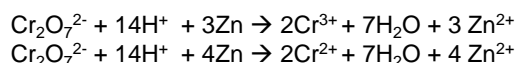
Addition of alkali will remove the H^+ ions and, by application of le Chatelier, push the equilibrium to the chromate.

This is not a redox reaction as both the chromate and dichromate ions have an oxidation number of +6. This is an acid base reaction.



Reducing Chromium

Cr^{3+} (green) and then Cr^{2+} (blue) are formed by reduction of $\text{Cr}_2\text{O}_7^{2-}$ (orange) by the strong reducing agent zinc in (HCl) acid solution. Fe^{2+} is a less strong reducing agent and will only reduce the dichromate to Cr^{3+} .



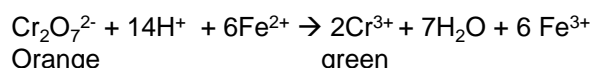
$\text{Cr}_2\text{O}_7^{2-}$ (orange) Cr^{3+} (green)



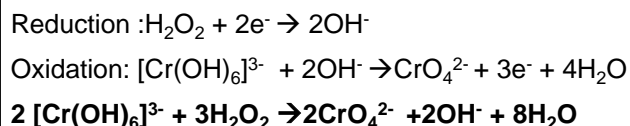
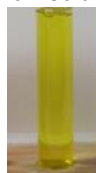
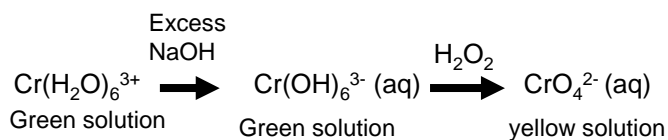
Keeping the zinc/dichromate under a hydrogen atmosphere is needed to reduce to Cr^{2+} . This picture shows Cr^{2+} formed under a hydrogen atmosphere



The Fe^{2+} and $\text{Cr}_2\text{O}_7^{2-}$ in acid solution reaction can be used as a quantitative redox titration. This does not need an indicator.



Chromium compounds can be oxidised by using the **oxidising agent** hydrogen peroxide.



Half equations in alkaline conditions:

These are more difficult to do than half equations under acidic conditions. The easiest way of doing it is to balance as if under acidic conditions then add OH⁻ ions to both sides to convert to alkaline.

For change Cr(OH)₆³⁻ → CrO₄²⁻

Add H₂O to balance O: [Cr(OH)₆]³⁻ → CrO₄²⁻ + 2H₂O + 3e⁻

Add H⁺ to balance H: [Cr(OH)₆]³⁻ → CrO₄²⁻ + 2H₂O + 2H⁺ + 3e⁻

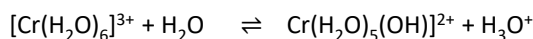
Add OH⁻ to both sides to cancel out H⁺: [Cr(OH)₆]³⁻ + 2OH⁻ → CrO₄²⁻ + 2H₂O + 2H⁺ + 2OH⁻ + 3e⁻

[Cr(OH)₆]³⁻ + 2OH⁻ → CrO₄²⁻ + 3e⁻ + 4H₂O

Reactions of the Cr³⁺_(aq) ion

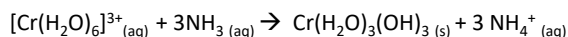
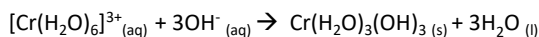
Addition of NaOH and NH₃

The Cr³⁺ (aq) ion is really the complex ion [Cr(H₂O)₆]³⁺ (aq). It should appear as a red-blue solution but normally appears green because of hydrolysis reaction below



Cr(H₂O)₅(OH)²⁺

Addition of **limited amounts of sodium hydroxide or ammonia** to this ion will result in the **green precipitate** of Chromium (III) hydroxide being formed.



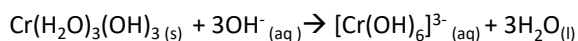
A few drops NaOH



A little more NaOH

Reaction with excess OH⁻

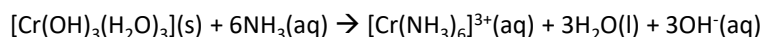
With excess NaOH, the Cr hydroxides dissolve.
Cr becomes [Cr(OH)₆]³⁻ (aq) green solution



[Cr(OH)₆]³⁻

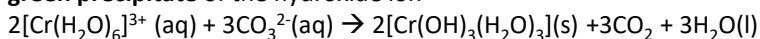
Excess NH₃

Addition of excess ammonia will result in the green hydroxide precipitate dissolving to form a purple solution

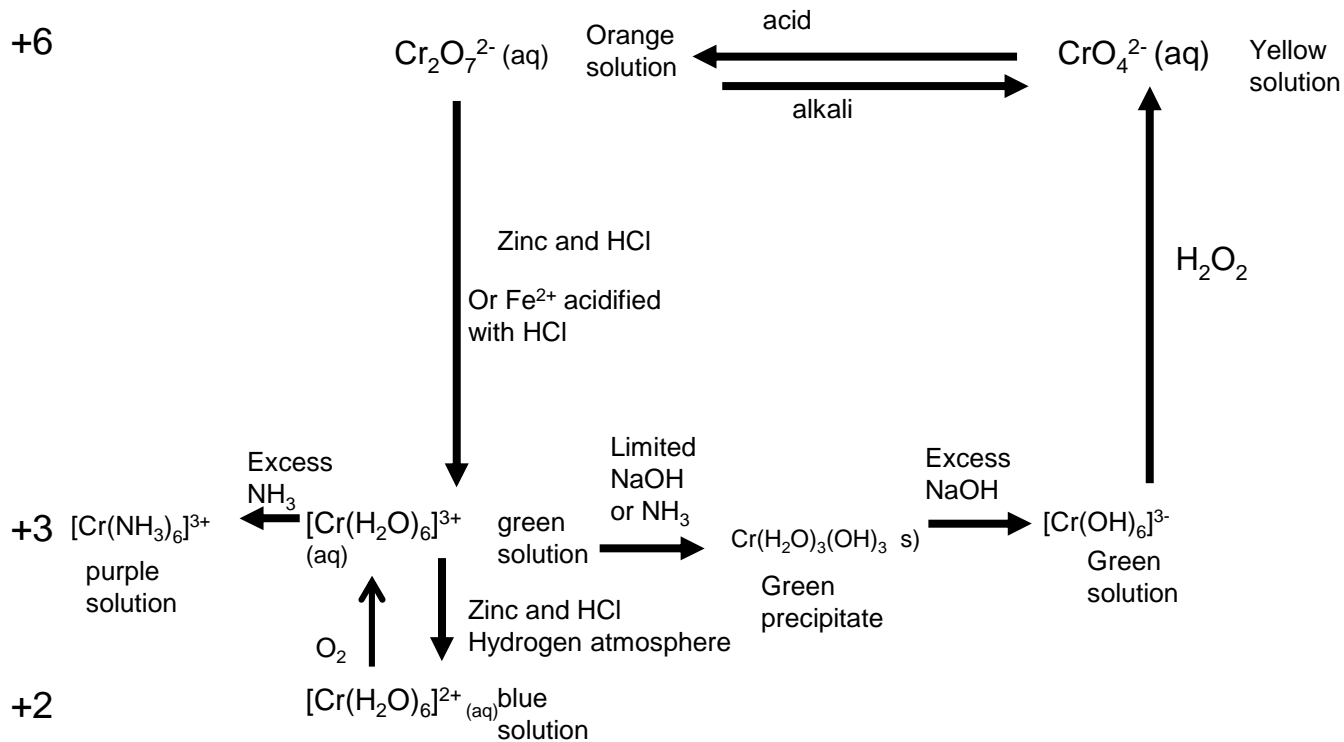


Addition of sodium carbonate

Like other 3⁺ ions the chromium decomposes the carbonate to give carbon dioxide and the **green precipitate** of the hydroxide ion

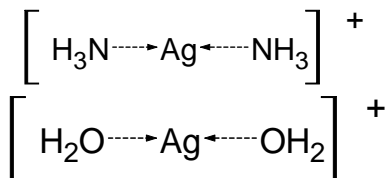


Chromium summary



Silver Chemistry

Ag⁺ commonly forms **linear** complexes
 e.g. [Ag(H₂O)₂]⁺ [Ag(NH₃)₂]⁺,
 [Ag(S₂O₃)₂]³⁻ and [Ag(CN)₂]⁻
 All are colourless solutions.



Silver behaves like the transition metals in that it can form complexes and can show catalytic behaviour (although it adsorbs too weakly for many examples).

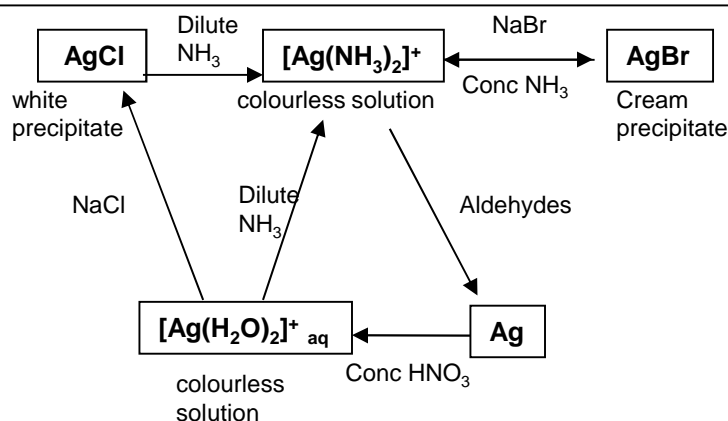
Silver is unlike the transition metals in that it does not form coloured compounds and does not have variable oxidation states.

Silver complexes all have a +1 oxidation state with a full 4d subshell (4d¹⁰). As it is 4d¹⁰ in both its atom and ion, it does not have a partially filled d subshell and so is not a transition metal by definition. It is not therefore able to do electron transitions between d orbitals that enable coloured compounds to occur.

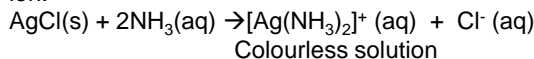
Reactions of Halides with silver nitrate

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

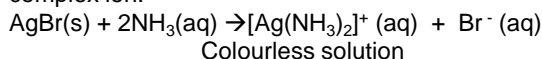
The silver halide precipitates can be treated with ammonia solution to help differentiate between them if the colours look similar:



Silver chloride dissolves in **dilute ammonia** to form a complex ion.

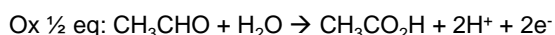
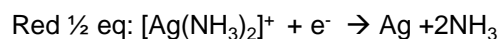


Silver bromide dissolves in **concentrated ammonia** to form a complex ion.



Silver iodide does not react with ammonia – it is too insoluble.

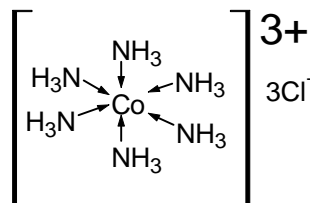
[Ag(NH₃)₂]⁺ is used in Tollen's reagent to distinguish between aldehydes and ketones. Aldehydes reduce the silver in the Tollen's reagent to silver.



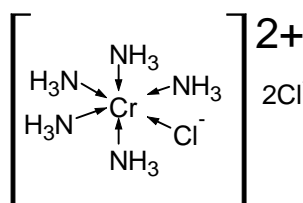
Using silver nitrate to work out formulae of chloride containing complexes

Sometimes a compound containing a complex may have Cl⁻ ions acting as ligands inside the complex and Cl⁻ ions outside the complex attracted ionically to it. If silver nitrate is added to such a compound it will only form the silver chloride precipitate with the free chloride ions outside of the complex.

e.g. Co(NH₃)₆Cl₃ reacts on a 1:3 mole ratio with silver nitrate as there are three free Cl⁻ ions. So all 3 Cls are outside the complex.



e.g. Cr(NH₃)₅Cl₃ reacts on a 1:2 mole ratio with silver nitrate as there are two free Cl⁻ ions. So 1 Cl is a ligand and 2 are outside the complex.



e.g. Cr(NH₃)₄Cl₃ reacts on a 1:1 mole ratio with silver nitrate as there is one free Cl⁻ ion. So 2 Cl's are ligands and 1 is outside the complex.

