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	$VO_2^+_{(aq)} + 2H^+_{(aq)} + e^- \rightarrow VO^{2+}_{(aq)} + H_2O$	+1.00 V
+4	VO^{2+}	BLUE	$VO^{2+}(aq + 2H^+(aq) + e^- \rightarrow V^{3+}_{(aq)} + H_2O$	+0.34 V
+3	V^{3+}	GREEN	$V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$	- 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.

$$Zn^{2+} + 2e^- \rightarrow Zn \quad E = -0.76V$$

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

$$Sn^{2+} + 2e^- \rightarrow \quad Sn \quad E=-0.136V$$
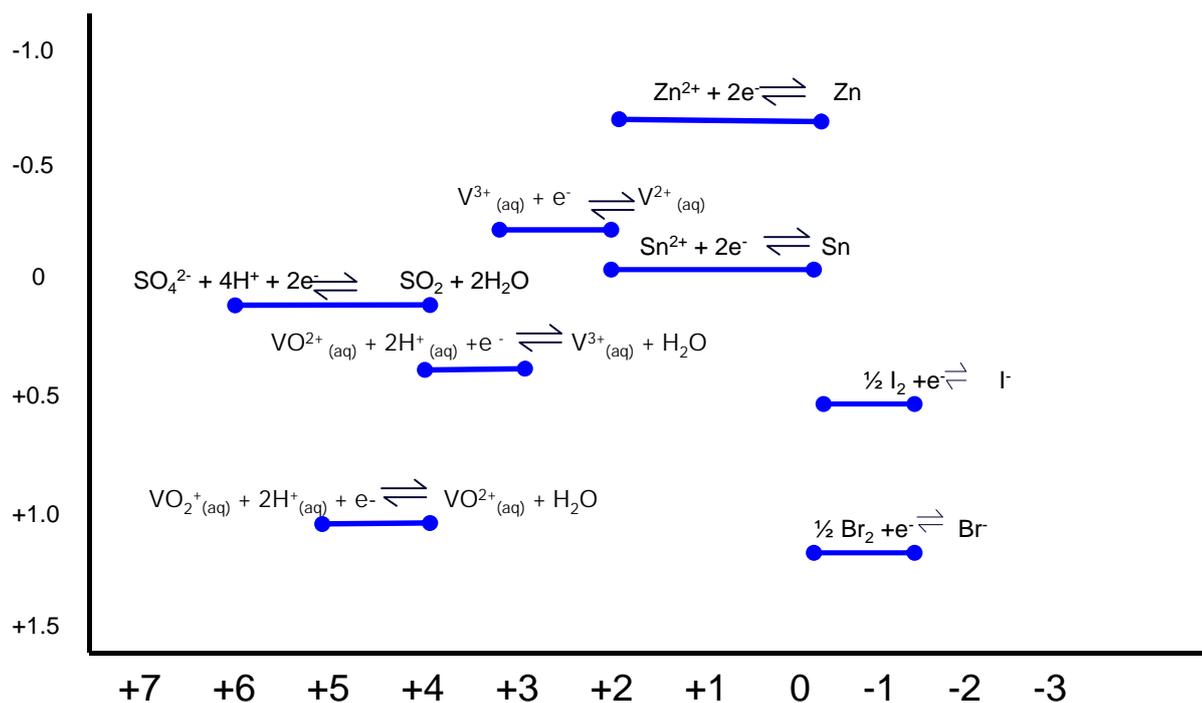
Tin metal will only reduce the vanadium from +5 to the +3 state

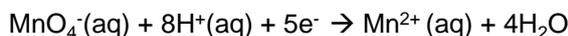Similarly iodide ions will reduce the vanadium from +5 to the +3 state

Manganese

Manganese has 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

$Mn^{2+}/ [Mn(H_2O_6)]^{2+}$ O.N. 2 very pale pink solution

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

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$$

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.

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$
Purple   colourless
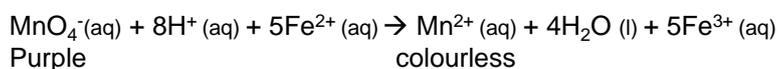
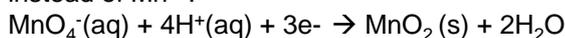The purple colour of manganate can make it difficult to see the bottom of meniscus in the burette.

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.

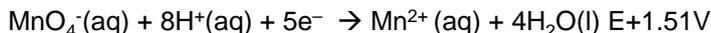Only **use dilute sulfuric acid** for manganate titrations.

Insufficient volumes of sulfuric acid will mean the solution is not acidic enough and MnO_2 will be produced instead of Mn^{2+}.
$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O$
The brown MnO_2 will mask the colour change and lead to a greater (inaccurate) volume of manganate being used in the titration.
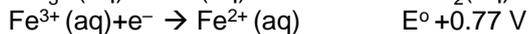Using a weak acid like ethanoic acid would have the same effect as it cannot supply the large amount of hydrogen ions needed ($8H^+$).

It cannot be **conc HCl** as the Cl^- ions would be oxidised to Cl_2 by MnO_4^- as the E^o MnO_4^-/Mn^{2+} > E^o Cl_2/Cl^-
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ E+1.51V
$Cl_2(aq) +2e^- \rightarrow 2Cl^-(aq)$ E +1.36V
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^o NO_3^-/HNO_2 > E^o Fe^{3+}/Fe^{2+}
$NO_3^-(aq) + 3H^+(aq) + 2e^- \rightarrow HNO_2(aq) + H_2O(l)$ E^o +0.94V
$Fe^{3+}(aq)+e^- \rightarrow Fe^{2+}(aq)$ E^o +0.77 V
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 100cm^3 acid. The solution formed contains Fe(II) ions.
10cm^3 portions of this solution are titrated with potassium manganate (VII) solution of 0.02M.
9.80cm^3 of $KMnO_4$ were needed to react with the solution containing the iron.
What is the percentage of Iron by mass in the nail?

$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5Fe^{2+} \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O + 5Fe^{3+}$
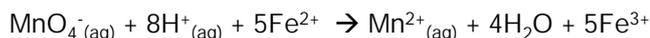
Step1 : find moles of $KMnO_4$
moles = conc x vol
$$0.02 \times 9.8/1000$$
$$= 1.96 \times 10^{-4} \text{ mol}$$

Step 2 : using balanced equation find moles Fe^{2+} in 10cm^3
= moles of $KMnO_4$ x 5
$$= 9.8 \times 10^{-4} \text{ mol}$$

Step 3 : find moles Fe^{2+} in 100cm^3
$$= 9.8 \times 10^{-4} \text{ mol} \times 10$$
$$= 9.8 \times 10^{-3} \text{ mol}$$

Step 4 : find mass of Fe in 9.8×10^{-3} mol
mass= moles x RAM = $9.8 \times 10^{-3} \times 55.8 = 0.547$g

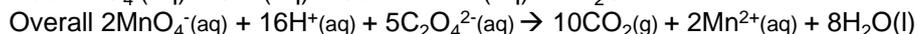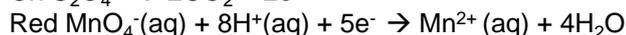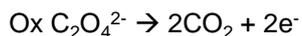Step 5 : find % mass
%mass = 0.547/2.41 x100
$$= 22.6\%$$

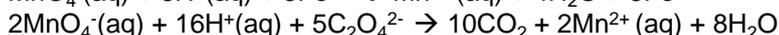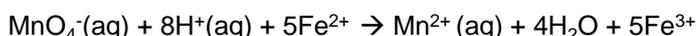**Other useful manganate titrations**

With hydrogen peroxide

Ox $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$
Red $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$
Overall $2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2 \rightarrow 5O_2 + 2Mn^{2+}(aq) + 8H_2O$

With ethanedioate

Ox $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$
Red $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$
Overall $2MnO_4^-{}_{(aq)} + 16H^+{}_{(aq)} + 5C_2O_4^{2-}{}_{(aq)} \rightarrow 10CO_{2(g)} + 2Mn^{2+}{}_{(aq)} + 8H_2O(l)$
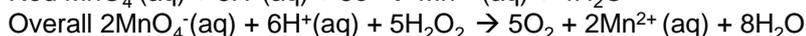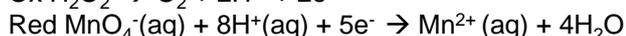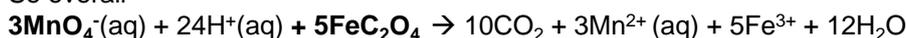
The reaction between MnO_4^- and $C_2O_4^{2-}$ is slow to begin with (as the reaction is between two negative ions). To do as a titration the conical flask can be heated to 60° C to speed up the initial reaction.

With Iron (II) ethanedioate both the Fe^{2+} and the $C_2O_4^{2-}$ react with the MnO_4^-
1MnO_4^- reacts with 5Fe^{2+} and 2 MnO_4^- reacts with 5$C_2O_4^{2-}$

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+} \rightarrow Mn^{2+}(aq) + 4H_2O + 5Fe^{3+}$
$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-} \rightarrow 10CO_2 + 2Mn^{2+}(aq) + 8H_2O$
So overall
$3MnO_4^-$(aq) + 24H$^+$(aq) + 5FeC$_2$O$_4$ $\rightarrow 10CO_2 + 3Mn^{2+}(aq) + 5Fe^{3+} + 12H_2O$

So overall the ratio is **3** MnO_4^- to **5** FeC_2O_4

A 1.412 g sample of impure $FeC_2O_4.2H_2O$ was dissolved in an excess of dilute sulphuric acid and made up to 250 cm^3 of solution. 25.0 cm^3 of this solution decolourised 23.45 cm^3 of a 0.0189 mol dm^{-3} solution of potassium manganate(VII).
What is the percentage by mass of $FeC_2O_4.2H_2O$ in the original sample?

Step1 : find moles of $KMnO_4$
moles = conc x vol
$$0.0189 \times 23.45/1000$$
$$= 4.43 \times 10^{-4} \text{ mol}$$

Step 2 : using balanced equation find moles $FeC_2O_4.2H_2O$ in 25cm^3
= moles of $KMnO_4$ x 5/3 (see above for ratio)
$$= 7.39 \times 10^{-4} \text{ mol}$$

Step 3 : find moles $FeC_2O_4.2H_2O$ in 250 cm^3
$$= 7.39 \times 10^{-4} \text{ mol} \times 10$$
$$= 7.39 \times 10^{-3} \text{ mol}$$

Step 4 : find mass of $FeC_2O_4.2H_2O$ in 7.39×10^{-3} mol
mass= moles x Mr = $7.39 \times 10^{-3} \times 179.8 = 1.33$g

Step 5 ; find % mass
%mass = 1.33/1.412 x100
$$= 94.1\%$$

Reaction of $[Mn(H_2O_6)]^{2+}$ 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.

$[Mn(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Mn(H_2O)_4(OH)_{2\ (s)} + 2H_2O_{(l)}$

$[Mn(H_2O)_6]^{2+}_{(aq)} + 2NH_{3\ (aq)} \rightarrow Mn(H_2O)_4(OH)_{2\ (s)} + 2NH_4^+_{(aq)}$

MnO_4^-

Fe^{2+}
$C_2O_4^{2-}$
H_2O_2

$[Mn(H_2O)_6]^{2+}$ $\xrightarrow{\text{Few drops } OH^- \text{ or } NH_3}$ $Mn(OH)_2(H_2O)_4$ $\xrightarrow{\text{Air or } H_2O_2}$ $Mn(OH)_3(H_2O)_3$

very pale pink sol H^+ light brown ppt   dark brown ppt
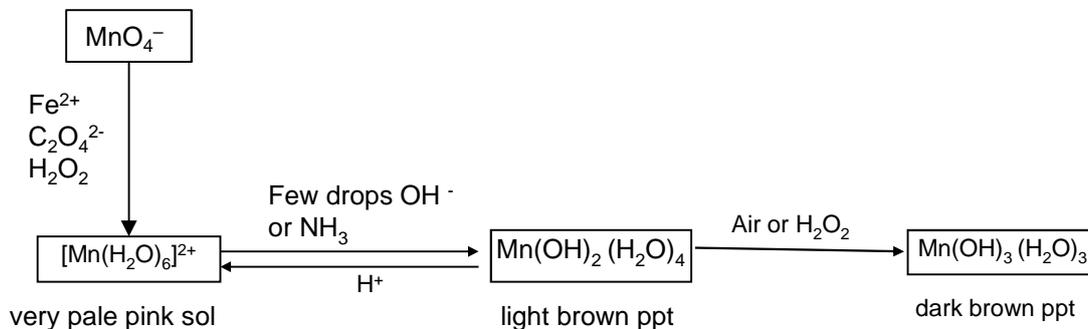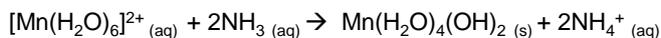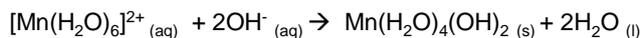
Cobalt reactions.
Cobalt two main oxidation states are +2 and +3

Oxidation of Cobalt

$[Co(H_2O)_6]^{2+}$ (aq) $\xrightarrow{\text{little } OH^- \text{ or } NH_3}$ $Co(H_2O)_4(OH)_2$ (s) $\xrightarrow{O_2}$ $Co(H_2O)_3(OH)_3$ (s)
brown precipitate

pink solution   blue precipitate

$\downarrow$ Excess NH_3

$[Co(NH_3)_6]^{2+}$ (aq) $\xrightarrow{O_2}$ $[Co(NH_3)_6]^{3+}$ (aq) + e^-
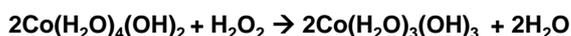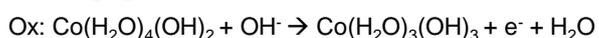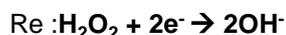
yellow solution   Brown solution

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:- **$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$**

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

Overall $4[Co(NH_3)_6]^{2+} O_2 + 2H_2O \rightarrow 4[Co(NH_3)_6]^{3+} + 4OH^-$

The H_2O_2 half equation for these reactions is

Re :**$H_2O_2 + 2e^- \rightarrow 2OH^-$**

Ox: $Co(H_2O)_4(OH)_2 + OH^- \rightarrow Co(H_2O)_3(OH)_3 + e^- + H_2O$

$2Co(H_2O)_4(OH)_2 + H_2O_2 \rightarrow 2Co(H_2O)_3(OH)_3 + 2H_2O$
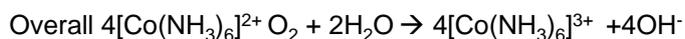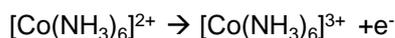
Copper Chemistry

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

$$Cu^{2+} \; [Ar] \; 4s^03d^9 \qquad\qquad Cu^+ \; [Ar] \; 4s^03d^{10}$$
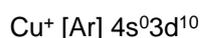
Copper(I) compounds are colourless in solution. In Cu^+ ions the 3d sub shell is full e.g.$3d^{10}$. There is no space for electrons to transfer, so there is not an energy transfer equal to that of visible light.
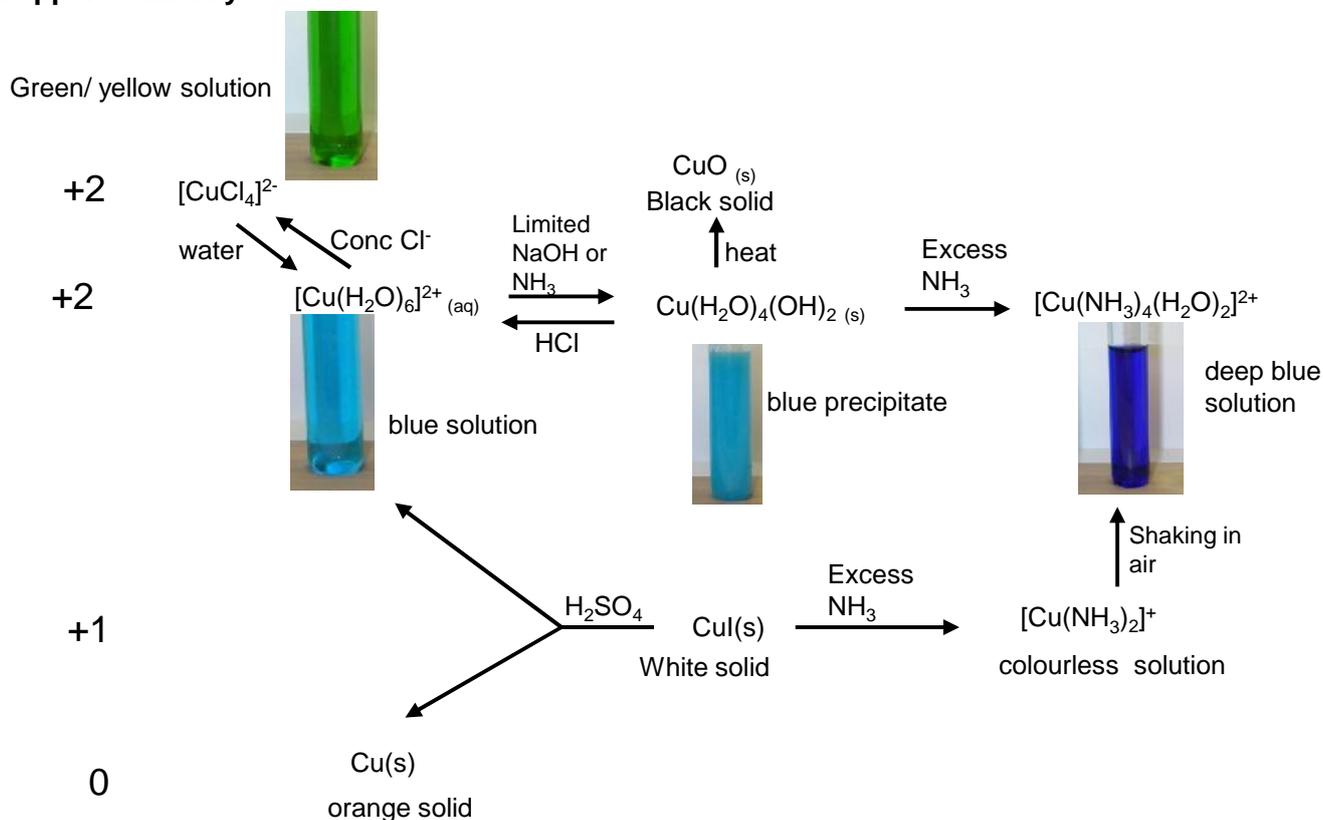
Disproportionation of copper(I) iodide

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

$$2Cu^+ \rightarrow \; Cu + Cu^{2+}$$

$Cu^+(aq) + e^- \rightarrow Cu(s) \; E^o = +0.52 \; V$
$Cu^{2+}{}_{(}aq) + e^- \rightarrow Cu^+(aq) \; E^o = +0.15 \; V$
So E^o cell = 0.52 – 0.15 = +0.37 V
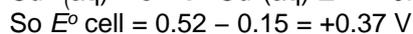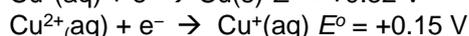
As E^o Cu^+/Cu > E^o Cu^{2+}/Cu^+ and Ecell has a positive value of +0.37V , Cu^+ disproportionates from +1 oxidation state to 0 in Cu and +2 in Cu^{2+}

Copper Summary

Green/ yellow solution

+2 $[CuCl_4]^{2-}$

water   Conc Cl⁻

+2 $[Cu(H_2O)_6]^{2+}$ (aq)

HCl

Limited NaOH or NH₃

$CuO_{(s)}$
Black solid

heat

$Cu(H_2O)_4(OH)_{2\;(s)}$

blue solution

blue precipitate

Excess NH₃

$[Cu(NH_3)_4(H_2O)_2]^{2+}$

deep blue solution

Shaking in air

H_2SO_4

+1   CuI(s)
White solid

Excess NH₃

$[Cu(NH_3)_2]^+$
colourless solution

0   Cu(s)
orange solid

Chromium Chemistry

Chromium has three main oxidations 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 $Cr_2O_7^{2-}$ ions both have oxidation states of +6. They can be converted from one to the other by the following equilibrium reaction.

$$2\ CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

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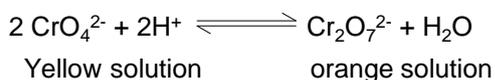
Addition of acid will by application of le Chatelier push the equilibrium to the dichromate.

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 $Cr_2O_7^{2-}$ (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+}.
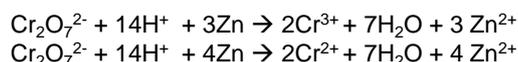
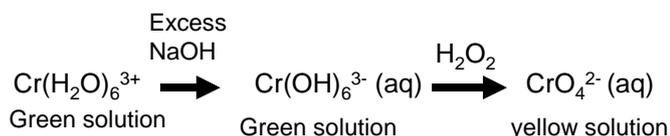$Cr_2O_7^{2-}$ (orange) Cr^{3+} (green)

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

$$Cr_2O_7^{2-} + 14H^+ + 3Zn \rightarrow 2Cr^{3+} + 7H_2O + 3\ Zn^{2+}$$
$$Cr_2O_7^{2-} + 14H^+ + 4Zn \rightarrow 2Cr^{2+} + 7H_2O + 4\ Zn^{2+}$$

The Fe^{2+} and $Cr_2O_7^{2-}$ in acid solution reaction can be used as a quantitative redox titration. This does not need an indicator.

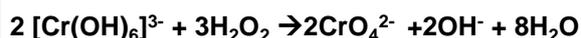$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6\ Fe^{3+}$$
Orange   green
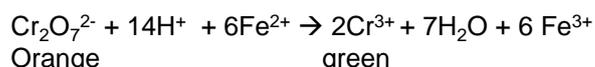
Chromium compounds can be oxidised by using the **oxidising agent** hydrogen peroxide.

$$Cr(H_2O)_6^{3+} \xrightarrow{\text{Excess NaOH}} Cr(OH)_6^{3-} \text{ (aq)} \xrightarrow{H_2O_2} CrO_4^{2-} \text{ (aq)}$$

Green solution   Green solution   yellow solution

Reduction : $H_2O_2 + 2e^- \rightarrow 2OH^-$

Oxidation: $[Cr(OH)_6]^{3-} + 2OH^- \rightarrow CrO_4^{2-} + 3e^- + 4H_2O$

$2\ [Cr(OH)_6]^{3-} + 3H_2O_2 \rightarrow 2CrO_4^{2-} + 2OH^- + 8H_2O$

Reactions of the Cr^{3+} $_{(aq)}$ ion

Addition of NaOH and NH$_3$

The Cr^{3+} (aq) ion is really the complex ion $[Cr(H_2O)_6]^{3+}$ (aq). It should appear as a red-blue solution but normally appears green because of hydrolysis reaction below

$$[Cr(H_2O)_6]^{3+} + H_2O \rightleftharpoons Cr(H_2O)_5(OH)]^{2+} + H_3O^+$$
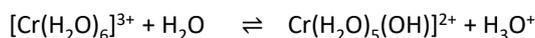
$Cr(H_2O)_5(OH)]^{2+}$

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

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

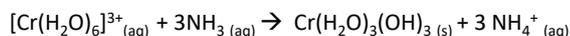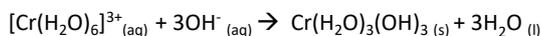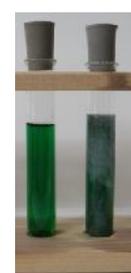$[Cr(H_2O)_6]^{3+}_{(aq)} + 3NH_{3\,(aq)} \rightarrow Cr(H_2O)_3(OH)_{3\,(s)} + 3\,NH_4^+_{(aq)}$

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

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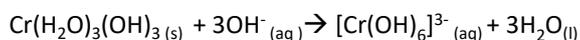
$[Cr(OH)_6]^{3-}$

Excess NH$_3$

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

$[Cr(OH)_3(H_2O)_3](s) + 6NH_3(aq) \rightarrow [Cr(NH_3)_6]^{3+}(aq) + 3H_2O(l) + 3OH^-(aq)$
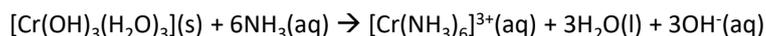
Addition of sodium carbonate

Like other $^{3+}$ ions the chromium decomposes the carbonate to give carbon dioxide and the **green precipitate** of the hydroxide ion
$2[Cr(H_2O)_6]^{3+}$ (aq) $+ 3CO_3^{2-}$(aq) $\rightarrow 2[Cr(OH)_3(H_2O)_3](s) + 3CO_2 + 3H_2O(l)$

Chromium summary

+6 $Cr_2O_7{}^{2-}$ (aq)   Orange solution   ← acid — $CrO_4{}^{2-}$ (aq)   Yellow solution

       — alkali →

Zinc and HCl

Or Fe^{2+} acidified with HCl

H_2O_2

Limited NaOH or NH_3 Excess NaOH

Excess NH_3

+3 $[Cr(NH_3)_6]^{3+}$ ← $[Cr(H_2O)_6]^{3+}$ (aq)   green solution   → $Cr(H_2O)_3(OH)_3$ (s)   → $[Cr(OH)_6]^{3-}$
purple solution   Green precipitate   Green solution

O_2 Zinc and HCl Hydrogen atmosphere

+2 $[Cr(H_2O)_6]^{2+}$ (aq) blue solution
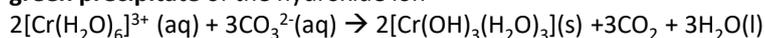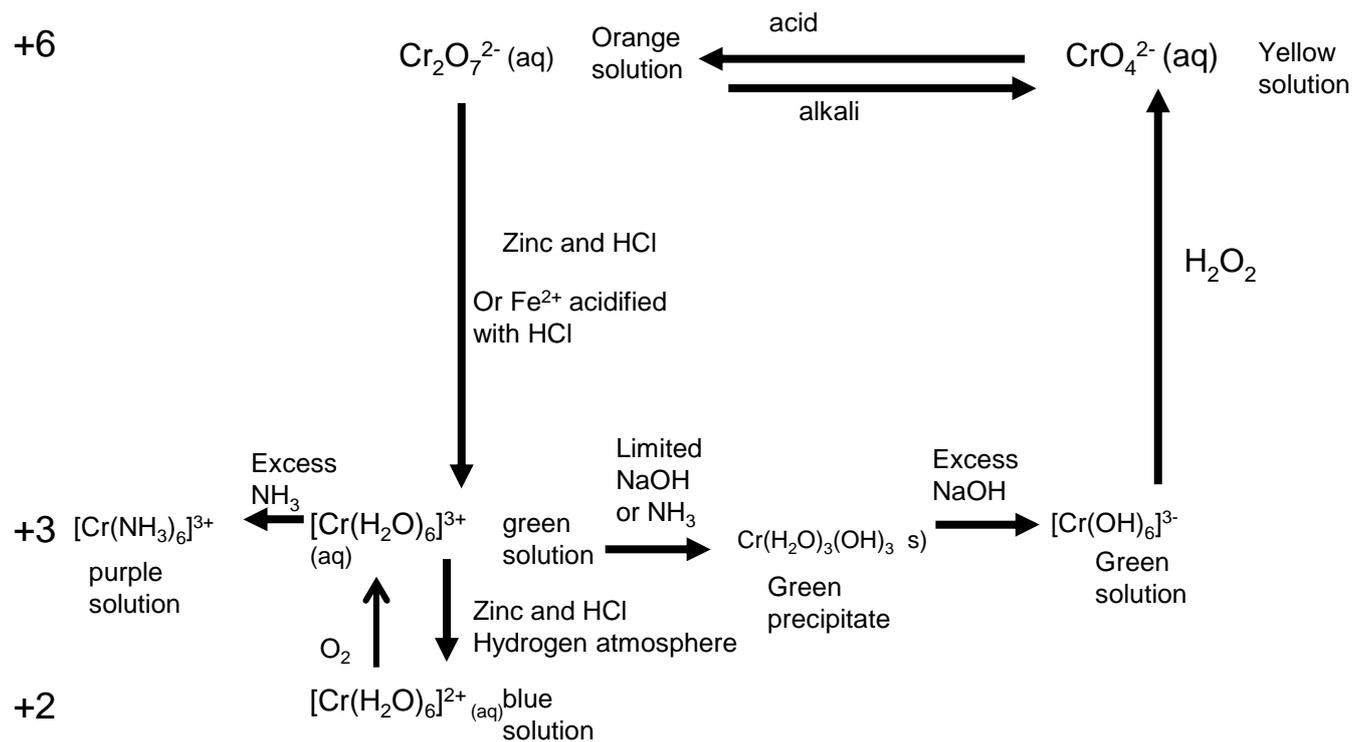
Silver Chemistry

Ag$^+$ commonly forms **linear** complexes
e.g. $[Ag(H_2O)_2]^+$ $[Ag(NH_3)_2]^+$,
$[Ag(S_2O_3)_2]^{3-}$ and $[Ag(CN)_2]^-$
All are colourless solutions.

$$\left[H_3N \text{----}\rightarrow Ag \leftarrow\text{----} NH_3 \right]^+$$

$$\left[H_2O \text{----}\rightarrow Ag \leftarrow\text{----} OH_2 \right]^+$$
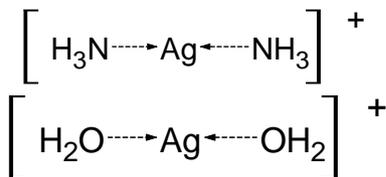
Silver behaves like the transition metals in that it can form complexes and can show catalytic behaviour (although it adsorbs too weakly for many examples).
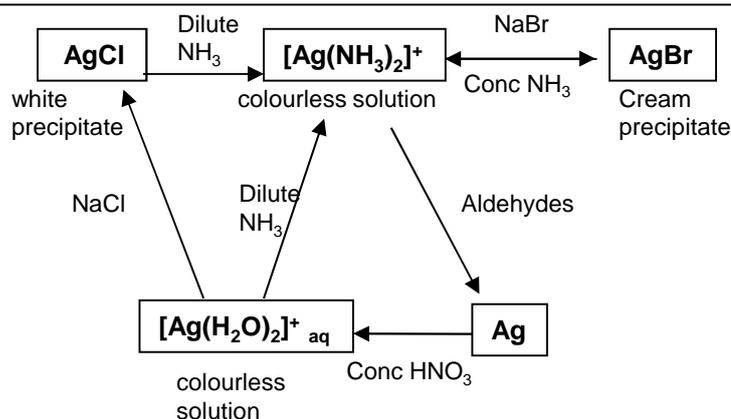
Silver is unlike the transition metals in that it does not form coloured compounds and does not have variable oxidation states.

Silver complexes all have a +1 oxidation state with a full 4d subshell (4d^{10}). As it is 4d^{10} 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
$Ag^+(aq) + Cl^- (aq) \rightarrow AgCl(s)$
Bromides produce a cream precipitate
$Ag^+(aq) + Br^- (aq) \rightarrow AgBr(s)$
Iodides produce a pale yellow precipitate
$Ag^+(aq) + I^- (aq) \rightarrow AgI(s)$
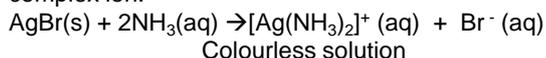
The silver halide precipitates can be treated with ammonia solution to help differentiate between them if the colours look similar:

AgCl — Dilute NH$_3$ → **[Ag(NH$_3$)$_2$]$^+$** — NaBr / Conc NH$_3$ → **AgBr**
white precipitate — colourless solution — Cream precipitate

NaCl / Dilute NH$_3$ / Aldehydes
[Ag(H$_2$O)$_2$]$^+$ $_{aq}$ — colourless solution ← Conc HNO$_3$ — **Ag**

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.

$[Ag(NH_3)_2]^+$ is used in Tollen's reagent to distinguish between aldehydes and ketones . Aldehydes reduce the silver in the Tollen's reagent to silver.

Red ½ eq: $[Ag(NH_3)_2]^+ + e^- \rightarrow Ag + 2NH_3$

Ox ½ eq: $CH_3CHO + H_2O \rightarrow CH_3CO_2H + 2H^+ + 2e^-$
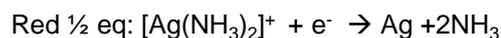
Using silver nitrate to work out formulae of chloride containing complexes

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(NH$_3$)$_6$Cl$_3$ 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.
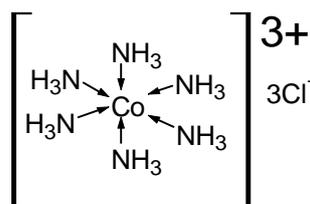
e.g. Cr(NH$_3$)$_5$Cl$_3$ reacts on a 1:2 mole ratio with silver nitrate as there are two free Cl$^-$ ions. So 1 Cl is a ligand and 2 are outside the complex.
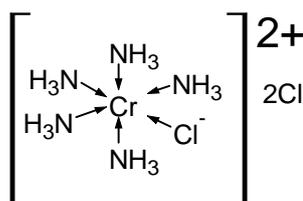
e.g. Cr(NH$_3$)$_4$Cl$_3$ reacts on a 1:1 mole ratio with silver nitrate as there is one free Cl$^-$ ion. So 2 Cl's are ligands and 1 is outside the complex.

$$\left[\begin{array}{c} NH_3 \\ H_3N \searrow \downarrow \swarrow NH_3 \\ Co \\ H_3N \nearrow \uparrow \nwarrow NH_3 \\ NH_3 \end{array} \right]^{3+} \quad 3Cl^-$$

$$\left[\begin{array}{c} NH_3 \\ H_3N \searrow \downarrow \swarrow NH_3 \\ Cr \\ H_3N \nearrow \uparrow \nwarrow Cl^- \\ NH_3 \end{array} \right]^{2+} \quad 2Cl^-$$

$$\left[\begin{array}{c} NH_3 \\ H_3N \searrow \downarrow \swarrow NH_3 \\ Cr \\ H_3N \nearrow \uparrow \nwarrow Cl^- \\ Cl^- \end{array} \right]^{+} \quad Cl^-$$