Chem Factsheet

www.curriculum-press.co.uk Number 75

The Chemistry of Chromium

To succeed in this topic you need to understand:
- the basics of transition metals (covered in Factsheet 28);
- the reactions of transition metal ions with hydroxides and ammonia (covered in Factsheet 46);
- the principles of oxidation and reduction (covered in Factsheet 11).

After working through this Factsheet you will:
- know the oxidation states of chromium;
- know that the +3 state is stable, while +6 is an oxidising state and +2 is a reducing state;
- understand the relationships between the principal compounds of chromium;
- know the acid-base character of the oxides;
- understand the reactions of $Cr^{3+}(aq)$ with $OH^-(aq)$, $NH_3(aq)$ and $CO_3^{2-}(aq)$;
- understand how to access the +6 oxidation state;
- know the interconversion of chromium(VI) compounds.

The element

Chromium (atomic number = 24) is the fourth member of the first series of d-block transition elements.

- Its electronic configuration is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$. This arrangement, in which each of the 3d orbitals is singly occupied, is more stable than the alternative $[Ar]\ 3d^4, 4s^2$.
- It is a hard metal with a bluish tinge, familiar as chromium plating on furniture and the trim of classic cars. The melting point is very high (1890 °C).

> ***Exam Hint*** *- Although chromium itself is not in A-level specifications, its aqueous chemistry is a popular topic.*

Oxidation states

> *The oxidation states of chromium are +2, +3 and +6, of which only +3 is stable.*

Principal compounds and ions are as follows.
- Cr^{II} The chromium(II) ion, Cr^{2+}. Its electronic configuration is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^4$.
- Cr^{III} Chromium(III) oxide, Cr_2O_3, chromium(III) hydroxide, $Cr(OH)_3$, the chromium(III) ion, Cr^{3+}, and various complex ions such as the hydrated chromium(III) ion, $[Cr(H_2O)_6]^{3+}$.
  The electronic configuration of the Cr^{3+} ion is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^3$.

> ***Remember*** *- Whenever ions are formed from atoms of transition elements, it is always the outer 4s electrons that are lost first.*

- Cr^{VI} Chromium(VI) oxide, CrO_3, the chromate(VI) ion, CrO_4^{2-}, and the dichromate(VI) ion, $Cr_2O_7^{2-}$.

> ***Exam Hint*** *- Never say that a chromate(VI) or a dichromate(VI) contains Cr^{6+} because this symbolises a non-existent ion. The correct abbreviation for chromium(VI), i.e. chromium in the +6 oxidation state, is Cr^{VI}.*

The +6 state

This is described as an 'oxidising state' because **most** species (i.e. molecules and ions) of chromium in this state have a tendency to become reduced to more stable chromium(III) species, usually the Cr^{3+} ion. The $Cr_2O_7^{2-}$ ion is particularly important: in acidic solution (dilute H_2SO_4 is usually used), its orange solution is reduced to a green solution of $Cr^{3+}(aq)$:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

Reducing agents which can be oxidised by dichromates(VI) include Fe^{2+} salts (to Fe^{3+} salts), sulphites (to sulphates) and ethanol (to ethanal).

> ***Remember*** *- Not all chromium(VI) species are oxidants. (A reaction will occur only if a mechanism is available.) In particular,* ***the chromate(VI) ion, CrO_4^{2-}, is not an oxidant.***

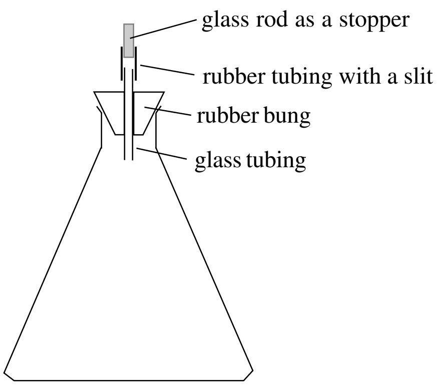
The +2 state

This is a reducing state - a remarkably powerful one.

Practical 1 - The action of air on Cr^{2+}

Prepare a chromium(II) compound in the absence of air by boiling a solution of potassium dichromate(VI) with zinc and dilute hydrochloric acid in a conical flask fitted with a bunsen valve (Fig 1).

Fig 1. A conical flask fitted with a bunsen valve



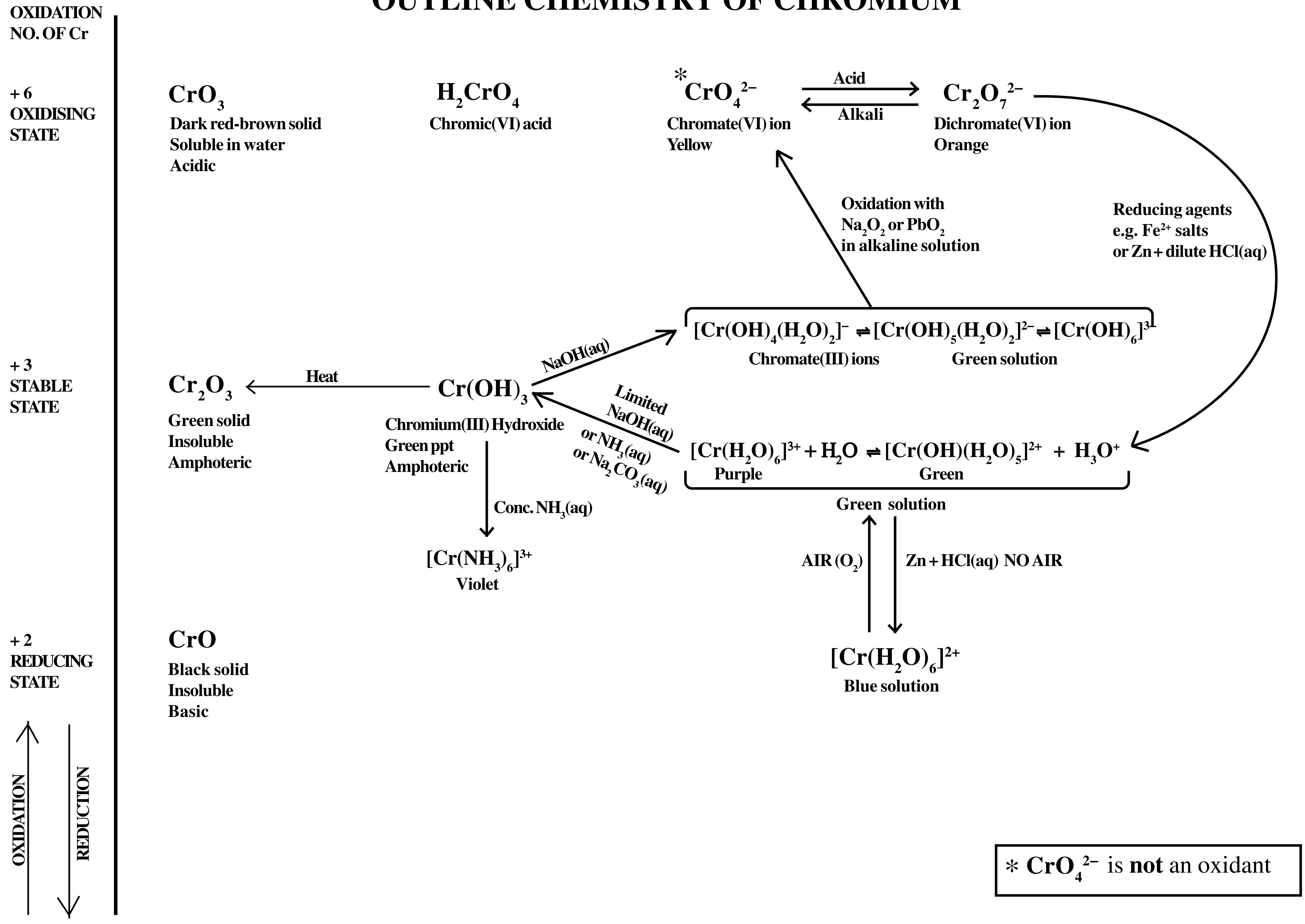
The solution changes colour from orange to green and then to sky blue as chromium is reduced from +6 to +3 and then to +2. Afterwards, remove the bunsen valve and shake the flask. The solution immediately changes from blue to green as oxygen from the air oxidises chromium(II) to chromium(III).

> ***Remember*** *- The most stable oxidation state of chromium is +3.*

Redox chart

On the redox chart of chromium (p2), the principal compounds and ions have been arranged in order of oxidation number.
- Any movement up the chart represents an oxidation process, for which an oxidising agent is required.
- Movement down the chart corresponds to reduction. For this, a reducing agent is needed, such as Zn and HCl(aq) in Practical 1.
- Movement across the chart is neither oxidation nor reduction, and is achieved with reagents such as water, dilute acids, NaOH(aq), $NH_3(aq)$ or $Na_2CO_3(aq)$.

OUTLINE CHEMISTRY OF CHROMIUM



* **CrO_4^{2-}** is **not** an oxidant

Oxides

Chromium forms three oxides.

- Chromium(II) oxide, CrO, a little known basic oxide.
- Chromium(III) oxide, Cr_2O_3, which is amphoteric, dissolving in acids to give chromium(III) salts and in alkalis to give chromates(III).
- Chromium(VI) oxide, CrO_3, which is acidic, dissolving in water to give chromic(VI) acid, H_2CrO_4, and in alkalis to give chromates(VI).

Chromium(III) hydroxide, $Cr(OH)_3$, like the oxide, is amphoteric. The nature of a hydroxide is usually the same as that of the corresponding oxide.

The acidity of oxides increases with oxygen content. (Some people say that acidity increases with oxidation number.)

Aqueous chemistry of chromium(III)

Hydrated chromium(III) ion

$[Cr(H_2O)_6]^{3+}$, named systematically as the hexaaquachromium(III) ion, is purple, but gives a turquoise coloured acidic solution.

Practical 2 - Hydrolysis of chromium(III) salts

Dissolve in water a purple chromium(III) salt, such as chrome alum, and test the solution with pH paper. Note the change in colour and the pH of the solution.

The hydrated chromium(III) ion can donate a proton from one of its coordinated water molecules to a molecule of solvent water:

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

An equilibrium is established containing both $[Cr(H_2O)_6]^{3+}$, which is purple, and $[Cr(OH)(H_2O)_5]^{2+}$, which is green. Consequently, the solution is bluish-green. It is also acidic, because $H_3O^+(aq)$ ions ("hydrogen ions") are formed, and the concentration of these is greater than that of $OH^-(aq)$ ions.

The reaction is known as an *acid-base reaction* or *deprotonation* because $[Cr(H_2O)_6]^{3+}$ behaves as an acid (proton donor) and H_2O as a base (proton acceptor).

Other molecules or ions, notably OH^-, NH_3 and CO_3^{2-} can also react as bases with $[Cr(H_2O)_6]^{3+}$, but these species are stronger bases than H_2O and further deprotonation can occur.

Practical 3 - Cr(III) salts with OH^-(aq)

Add dilute NaOH(aq) dropwise, with shaking, to a solution of a chromium(III) salt. A grey-green precipitate of hydrated chromium(III) hydroxide is formed at first. This dissolves in excess NaOH(aq) to give a grass-green solution of a chromate(III).

***Exam Hint -** Do not confuse a green chromate(III) with a yellow chromate(VI).*

Chromium(III) hydroxide is formed in an acid-base reaction in which three water molecules coordinated to Cr^{3+} each lose a proton. This can be represented by the equation:

$$[Cr(OH)(H_2O)_5]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Cr(OH)_3(H_2O)_3](s) + 2H_2O(l)$$

or

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

The dissolving of chromium(III) hydroxide in excess NaOH(aq) occurs by a continuation of the same process:

$$[Cr(OH)_3(H_2O)_3](s) + OH^-(aq) \rightleftharpoons [Cr(OH)_4(H_2O)_2]^-(aq) + H_2O(l)$$

$$[Cr(OH)_4(H_2O)_2]^-(aq) + OH^-(aq) \rightleftharpoons [Cr(OH)_5(H_2O)]^{2-}(aq) + H_2O(l)$$

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

An equilibrium is established in which the dominant ion is $[Cr(OH)_4(H_2O)_2]^-$ at low concentrations of OH^-, and $[Cr(OH)_6]^{3-}$ at high concentrations.

Practical 4 - Reverse changes

Add a dilute acid to a chromate(III) solution. Chromium(III) hydroxide is precipitated at first, and then dissolves in excess acid to give a bluish-green solution of a chromium(III) salt.

$H^+(aq)$ ions from the acid react with $OH^-(aq)$ ions (to give H_2O) so that the various equilibria are disturbed to the left hand side.

Practical 5 - Cr(III) salts with NH_3(aq)

Add dilute $NH_3(aq)$ dropwise, with shaking, to a solution of a chromium(III) salt. As with NaOH(aq), a grey-green precipitate of hydrated chromium(III) hydroxide is formed in an acid-base reaction:

$$[Cr(OH)(H_2O)_5]^{2+}(aq) + 2NH_3(aq) \rightleftharpoons [Cr(OH)_3(H_2O)_3](s) + 2NH_4^+(aq)$$

Now add *concentrated* $NH_3(aq)$. Although the precipitate is insoluble in dilute $NH_3(aq)$, it will partially dissolve in the concentrated reagent in a ligand substitution reaction to give a violet solution containing the hexaamminechromium(III) ion:

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

Practical 6 - Cr(III) salts with CO_3^{2-}(aq)

Add $Na_2CO_3(aq)$, with shaking, to a solution of a chromium(III) salt. Notice the formation of a grey-green precipitate of hydrated chromium(III) hydroxide, accompanied by effervescence. Collect the gas evolved in a squeezed out teat pipette and bubble it through limewater.

Again, there is an acid-base reaction but, when CO_3^{2-} ions accept protons, carbonic acid is not formed because of its instability. Instead, its decomposition products, carbon dioxide and water, are produced.

$$[Cr(OH)(H_2O)_5]^{2+}(aq) + CO_3^{2-}(aq) \rightarrow [Cr(OH)_3(H_2O)_3](s) + H_2O(l) + CO_2(g)$$

The addition of NaOH(aq), $NH_3(aq)$ or $Na_2CO_3(aq)$ to an aqueous solution of a chromium(III) salt gives an identical grey-green precipitate of hydrated chromium(III) hydroxide. In all cases, an acid-base (deprotonation) reaction occurs, in which the hydrated chromium(III) ion acts as an acid on the Brønsted-Lowry theory, i.e. a proton donor.

Now add excess $Na_2CO_3(aq)$ to the precipitate of chromium(III) hydroxide. For two reasons it will not dissolve.

- CO_3^{2-} is a weaker base than OH^-, so a chromate(III) ion cannot be formed.
- CO_3^{2-}, unlike NH_3, is not a ligand, so there can be no ligand substitution reaction.

***Remember -** With $Na_2CO_3(aq)$, M^{2+} ions form precipitates of metal carbonates, MCO_3, while M^{3+} ions give metal hydroxides, $M(OH)_3$, plus CO_2. Whatever the precipitate, it will **never** dissolve in excess reagent.*

Aqueous chemistry of chromium(VI)

Access to the +6 state

In general, it is difficult to oxidise Cr(III) compounds to Cr(VI) ones for two reasons.

- Most species containing Cr(VI) have a strong tendency to become reduced back to the Cr(III) state. However, the CrO_4^{2-} ion is not an oxidant, so this provides an obvious point of entry to the +6 oxidation level.
- Most oxidising agents operate only in acidic solution and, under these conditions, the CrO_4^{2-} ion is converted to $Cr_2O_7^{2-}$.

> *Oxidising agents which function in alkaline conditions and which are powerful enough to convert chromate(III) ions to chromate(VI) ions include sodium peroxide, hydrogen peroxide and lead(IV) oxide.*

Practical 7 - Preparation of sodium chromate(VI)
Pour a solution of a chromium(III) salt into a beaker and add NaOH(aq) with stirring until the initial precipitate of $Cr(OH)_3$ dissolves. Add Na_2O_2(s), stir and warm until the green solution changes colour to yellow. Boil the solution to decompose excess Na_2O_2, then cool it and allow Na_2CrO_4 to crystallise out.

$$2Cr^{3+}(aq) + 3O_2^{2-}(aq) + 4OH^-(aq) \rightarrow 2CrO_4^{2-}(aq) + 2H_2O(l)$$

Practice Questions

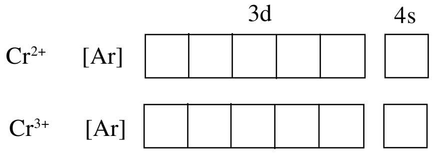
1 Acidified solutions containing the dichromate(VI) ion, $Cr_2O_7^{2-}$, and the dioxovanadium(V)ion, VO_2^+, are both orange and can both act as oxidising agents. Suggest a chemical means of distinguishing between them. Choose one test only, and describe what you would expect to see with each solution.

2 When crystals of an orange solid **A** were heated they decomposed exothermically, leaving a green solid **B** which dissolved in nitric acid to give a solution **C** and also in concentrated sodium hydroxide solution to give a solution **D**. When sodium hydroxide solution was added to **A**, it formed a yellow solution of **E** and gave off a pungent gas **F** which turned moist red litmus paper blue.
   (a) Write down the name and formula of **A**.
   (b) Identify **B**.
   (c) State the colours of solutions **C** and **D** and write down the formulae of their chromium containing ions.
   (d) Write an ionic equation for the formation of **E**.
   (e) Write an ionic equation for the formation of **F**.

3 When iron wire was added to an acidified solution of potassium dichromate(VI), the wire dissolved, the solution changed colour, and an odourless, neutral gas was evolved.
   (a) What colour change was observed?
   (b) *Construct* an ionic equation for the overall reaction between iron and dichromate(VI) ions. (You may omit state symbols.)
   (c) What gas was evolved?
   (d) In terms of electron transfer, how do you account for the formation of this gas?

4 There are three isomers of chromium(III) chloride-6-water, with the following formulae:
$[Cr(H_2O)_6]Cl_3$ $\quad$ $[CrCl(H_2O)_5]Cl_2.H_2O$ $\quad$ $[CrCl_2(H_2O)_4]Cl.2H_2O$
Suggest a chemical method for distinguishing between them.

5 (a) Using half-arrows to represent electrons, complete the following electronic configurations of the Cr^{2+} and Cr^{3+} ions.



   (b) Suggest why Cr^{2+} ions are readily oxidised to Cr^{3+} ions.

Interconversion of Cr(VI) compounds

Practical 8 - Preparation of sodium dichromate(VI)
Acidify the solution of sodium chromate(VI) prepared in Practical 7. Notice the colour change from yellow to orange.

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$$

Now make the solution alkaline again and see the colour revert to yellow.

$$Cr_2O_7^{2-}(aq) + 2OH^-(aq) \rightarrow 2CrO_4^{2-}(aq) + H_2O(l)$$

> ***Remember -*** *Chromates(VI) are yellow but dichromates(VI) are orange.*

Potassium dichromate(VI) is made by adding KCl(aq) to $Na_2Cr_2O_7$(aq) and crystallising the solution. Adding KOH to $K_2Cr_2O_7$ will give K_2CrO_4.

Answers

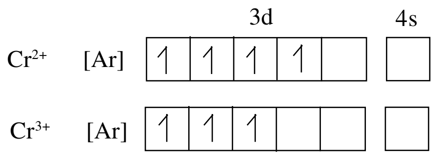
1 Add zinc (or other suitable metal) and boil. The $Cr_2O_7^{2-}$ solution changes colour to green and stays green. The VO_2^+ solution changes colour to green and then to blue (see Factsheet 46).

2 (a) Ammonium dichromate(VI), $(NH_4)_2Cr_2O_7$
   (b) Chromium(III) oxide, Cr_2O_3
   (c) **C** is green/blue-green/turquoise.
   It contains $[Cr(H_2O)_6]^{3+}$ (also $[Cr(OH)(H_2O)_5]^{2+}$).
   D is green.
   It contains $[Cr(OH)_4(H_2O)_2]^-$, $[Cr(OH)_5(H_2O)]^{2-}$ and $[Cr(OH)_6]^{3-}$.
   (d) $Cr_2O_7^{2-}(aq) + 2OH^-(aq) \rightarrow 2CrO_4^{2-}(aq) + H_2O(l)$
   (e) $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$

3 (a) From orange to dark green
   (b)
$$\left.\begin{array}{ll} Fe \rightarrow Fe^{3+} + 3e^- & \times 2 \\ Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O & \end{array}\right\}\text{add}$$
$$\Rightarrow 2Fe + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Fe^{3+} + 2Cr^{3+} + 7H_2O$$
   (c) Hydrogen
   (d) Some of the electrons lost by Fe as it dissolves are transferred to hydrogen ions from the acid: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

4 Only free Cl^- ions will react with $AgNO_3$(aq): not Cl^- ions which are coordinated to the central Cr^{3+} ion.
Weigh out equal masses of the three isomers, dissolve each in water, acidify with dilute HNO_3 and add excess $AgNO_3$(aq). Filter off the precipitated AgCl, wash, dry and weigh. The masses will be in the ratio 3:2:1.

5 (a)



   (b) 3d sub-shell electrons are split by ligands into two sets of d-orbitals. There are three orbitals in the lower energy set and two in the higher energy set. Cr^{3+} can have all its 3d electrons in the lower set, but Cr^{2+} must have at least one 3d electron in the upper set.

Acknowledgements: *This Factsheet was researched and written by John Brockington.* ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ChemistryFactsheets*** *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.* ***ISSN 1351-5136***