Advance warning

The following items needed for activities in this unit may not already be in your school, and might take a little time to obtain.

Activity	Item(s)	Essential/Optional	Typical quantity per experiment
SS1.1	Potassium iodate(VII) (periodate), KIO ₄	Essential	0.5g
	Colorimeter	Essential	
SS1.2	Spinach/spinach beet or rhubarb leaves	Essential	15g spinach leaves or 5g rhubarb leaves
SS2.2	The video 'The Steel Story' produced by Corus*	Optional	
SS5.1	Ammonium vanadate(V) (metavanadate), NH ₄ VO ₃	Essential	0.25g
SS5.2	Potassium sodium 2,3-dihydroxybutanedioate (potassium sodium tartrate or Rochelle salt)	Essential	2.5g
	Cobalt(II) chloride, CoCl ₂ .6H ₂ O	Essential	0.25g
SS5.3	Nickel(II) chloride, NiCl ₂ .6H ₂ O	Essential	1 g
	Ethylenediaminetetraacetic acid disodium salt (Na ₂ H ₂ edta)	Essential	0.5 g

* Current suppliers are listed on the Salters Advanced Chemistry Web Site.

Storyline: answers to assignments

1 For example, car bodies, steel girders for construction, cutlery, razor blades, boilers, mower blades, springs, paper clips, high-speed drill bits, fencing wire, door hinges, car tyre cords, drink cans, underwater gas pipes, etc.

2		Fe	С
	Number of moles in 100 g	1.68	0.37
	Mole %	82.0	18.0
	There are approximately 18 ca	arbon ato	ms in every 100
	atoms of product from a blast	furnace.	

3 a $S + 2e^- \rightarrow S^{2-}$

h

This is a reduction because the sulphur atom gains two electrons.

[Mg]	2+	* S * * S * * x *	2
(2.8)		(2.8.8)	

- 4 a It would be burnt as a fuel to keep down energy costs.b CO is poisonous. (It attaches itself to haemoglobin in the blood and prevents transport of oxygen around the body.)
 - cCalcium silicate(IV)CaSiO3Calcium phosphate(V) $Ca_3(PO_4)_2$
 - **d** CaO reacts with acids to form salts. It reacts with water to produce an alkaline solution containing calcium hydroxide.

 $CaO + H_2O \rightarrow Ca(OH)_2$

 P_4O_{10} reacts with bases to form salts. It reacts with water to produce an acidic solution containing phosphoric(V) acid.

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

- 5 a Silicon
 - **b** Phosphorus
 - **c** No. White phosphorus ignites spontaneously in air just above room temperature. Silicon is more stable in air and ignites at a much higher temperature.
 - **d** Sulphur would be oxidised late on in the oxygen blow, after the removal of phosphorus. It is also difficult to

remove completely. This is because it has an affinity for oxygen similar to iron at the high temperatures in the converter, but is present in much smaller amounts. So, at this late stage in the blow, large amounts of iron would be oxidised in preference to sulphur.

- **6 a** If the blow were stopped at the appropriate carbon concentration, the concentration of phosphorus (and possibly manganese) would be too high. It would be difficult to stop the blow at a precise carbon concentration.
 - **b** Individual batches of steel are produced to match precise customer specifications for the concentration of each element. Steel manufacture by a continuous process would be economical only if one type of steel were being produced. Otherwise, there would be a lot of wastage and accurate control of the composition would not be so easy.
- 7 A cell is set up between the steel and the attached metal. Electrons flow to the half-cell at the more positive potential. The iron half-cell with $E^{\circ} = -0.44$ V is at a more positive potential than the magnesium and zinc half-cells, and so electrons will flow from Mg and Zn to Fe²⁺. Magnesium and zinc are oxidised in preference to iron.

But the tin half-cell with $E^{\circ} = -0.14$ V is at a more positive potential than the iron half-cell. In this case, electrons will flow from the iron half-cell to the tin halfcell, so that iron is oxidised in preference to tin and rusting occurs more quickly.

- 8 a Bacteria which cause food spoilage are killed during heating. It is important to seal the hot food in an airtight container so that it is not recontaminated with bacteria from the air. It is also important that the can is full and as much air as possible is excluded, otherwise oxygen will react with some of the compounds in the food (eg fats will go rancid).
 - **b** To protect the iron can from the food inside and the conditions outside, and so prevent rusting.
 - **c** An electrochemical cell is set up between the tin and the iron in contact with moist air. The $Sn^{2+}(aq)/Sn(s)$

half-cell has a more positive electrode potential than the $Fe^{2+}(aq)/Fe(s)$ half-cell. Electrons will flow from the iron half-cell to the tin half-cell, and iron is oxidised in preference to tin.

Where the surface was scratched, the iron would act as a site of oxidation and the tin would act as a site of reduction. Thus, the can would rust quickly at the damaged areas.

- **d** Zinc is a reactive metal and is very susceptible to attack by acids – in fruit juices for example. Zinc ions would pass into the food and are toxic in high concentration. Tin is attacked more slowly by acids and tin ions are non-toxic.
- **9 a** They would know the exact composition of the scrap steel, which would help in planning how to adjust the composition of the new steel.

Activities: notes and answers to questions.

SS1.1 How much manganese is there in a paper clip?

Safety note Solid potassium iodate(VII) (periodate) KIO₄ and solid potassium manganate(VII) are both powerful oxidisers. They should not be allowed to come into contact with any combustible materials. Full information about other hazardous chemicals is given on the activity sheet.

Additional glassware required (per experiment)

1 dm³ graduated flask 250 cm³ graduated flask 25 cm³ pipette and two burettes

Comments

During the first part of the activity, the students convert all of the manganese in the paper clip (or similar item) into 100 cm^3 of a solution of potassium manganate(VII). It is important to use a freshly made-up solution of potassium iodate(VII) (periodate) KIO₄. The phosphoric(V) acid prevents the precipitation of iron(III) iodate(VII) and also removes the iron(III) colour by complex formation.

In the second part of the activity, students are asked to devise a method of finding the concentration of this solution using a colorimetric method. This involves producing a concentration/absorbance (or transmittance) calibration graph by preparing standard solutions of potassium manganate(VII) for use with a colorimeter. About five or six points should be adequate. The absorbance (or transmittance) of the solution from the paper clip can then be measured, its concentration read off the graph and the percentage of manganese in the paper clip determined.

Most steels contain less than 2% manganese and a typical value for the steel used in a paper clip is about 0.3%. Since the mass of manganese involved is very small, a more concentrated solution of potassium manganate(VII) is made up and then progressively diluted.

A suggested student method for the measurement of concentration is given below. Some teachers may prefer to give more guidance and provide students with at least one of the KMnO₄ solutions.

Mass of Mn in 0.2 g of steel containing 2% Mn = 0.004 g Mass of KMnO₄ produced by oxidation of 0.004 g Mn = 0.01149 g

- cost of melting scrap to compact it prior to dumping
 cost of storing radioactive steel until its activity decreased
- iron is a finite resource which should be conserved
- energy consumption in making new steel is much greater than that used to recycle scrap
- if diluted with other steel, should the diluted steel be used for general purposes or for specialist purposes away from the general public?
- an increase of 1 μSv is very small compared to the background radiation from natural sources
- any increase in average dosage of radiation should be avoided.
- **10** Students should be encouraged to check back through their own notes, or in textbooks to produce, say, six examples of catalysts.

Maximum concentration of KMnO₄ solution required = $0.01149 \text{ g in } 100 \text{ cm}^3$ = 0.1149 g dm^{-3}

- Accurately weigh out between 1.1 g and 1.2 g of potassium manganate(VII) and dissolve in 1.0 mol dm⁻³ sulphuric acid in a 1 dm³ volumetric flask. This corresponds to the solution which would be obtained from a paper clip containing 20% Mn (20% Mn solution).
- **2** Pipette 25 cm³ of this solution into a 250 cm³ volumetric flask and make up to the mark with distilled water. This corresponds to the solution which would be obtained from a paper clip containing 2% Mn (2% Mn solution). Set aside a sample of this solution to use in the colorimeter.
- 3 Fill a burette with the '2% Mn solution' and fill another burette with water. Make up 20 cm³ samples of solutions to correspond to 1%, 0.8%, 0.6%, 0.4%, 0.2% Mn solutions by using appropriate volumes from the two burettes.
- 4 Note the colorimeter readings given by each of the diluted potassium manganate(VII) solutions together with that produced by the paper clip solution. (It is important that the student thinks about rinsing the tube with appropriate solution between each reading.)
- **5** Draw a calibration graph of percentage of manganese in the paper clip against colorimeter reading. Read off the percentage of manganese in the paper clip.

Answers to the questions

- **a** If there is any manganese in a sample of steel a pink colour will appear when the steel sample has been dissolved in nitric acid and then oxidised with potassium iodate(VII).
- **b** An error in making up the original solution would affect all the other solutions obtained from it by dilution.
- **c** It is important to use carefully matched tubes for the water and potassium manganate(VII) solutions so that the pathlength of the light through the solution is the same in both cases.

The two tubes must be identical apart from the presence of potassium manganate(VII) in the second one. Thus, any difference in absorbance (or transmittance) between the two will be due to the potassium manganate(VII).

- d Students could be referred to Appendix 2 in the Individual Investigation: notes for students (Activities and Assessment Pack, page 361) which describes a *rule of thumb* for deciding how many significant figures ought to be quoted in a final answer.
- e The best filter to use is one which selects the region of wavelength of light most strongly absorbed by the solution. The filter is therefore a complementary colour to that of the solution.

_	Green
_	Blue/green
_	Blue
_	Violet
	- - -

f	Species	Oxidation state of Mn
	Mn	0
	Mn^{2+}	+2
	MnO_4^{-}	+7

Conversion of Mn to MnO_4^- is an oxidation because the oxidation state of manganese increases from 0 to +7.

g The solution obtained after the oxidation contains an excess of potassium iodate(VII) which is also a powerful oxidising agent. Hence, it is not possible to find the concentration of the potassium manganate(VII) by titration with a reducing agent.

SS.1.2 A redox titration

Safety note Information about hazardous chemicals is given on the activity sheet.

This is an interesting but complex titration in which both iron(II) and oxalate ions react with the potassium manganate(VII). If you prefer, it can be replaced by a more straightforward redox titration involving potassium manganate(VII).

Students will obtain high values in **14** for the iron(II) oxalate content of spinach, suggesting that other oxidisable material is also present.

- **a** The pink colour is caused by a slight excess of manganate(VII) ions.
- **b** The solution is heated to 60 °C because the initial rate of reaction is too slow at room temperature.

SS2.1 Why is blast furnace iron so impure?

- a Iron ore (containing iron(III) oxide Fe₂O₃) Coke (C) Limestone (CaCO₃) Air (source of O₂)
- **b** Conversion of iron ore to iron is a reduction because the oxidation state of iron changes from +3 to 0 (or the iron gains 3 electrons).

The main reducing agent is carbon monoxide (but, depending on the temperature, carbon also acts as a reducing agent in different parts of the furnace).

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d Carbon present in the iron produced comes from the coke.

e Silicon impurity comes from sand (SiO₂) present in the iron ore. Limestone is added to remove most of the SiO₂ present.

 $CaCO_3 \rightarrow CaO + CO_2$ $CaO + SiO_2 \rightarrow CaSiO_3$ calcium silicate'slag'

The molten slag floats on top of the denser molten iron and is tapped off separately.

f Sulphur – present in the coal used to make the coke (remember acid rain).
Phosphorus – phosphates are present in the iron ore.
Manganese – present in some iron ores.
(Some manganese is actually added to the iron ore fed into the blast furnace to aid separation of the molten iron from the slag.)

SS2.2 What changes occur during steelmaking?

This activity allows students to practise using a computer spreadsheet program. The data corresponds to the batch of steel shown on 'The Steel Story' video.

The following bar charts and graph were produced using the spreadsheet Excel.

Part 1: Plotting the changes

1 Changes in the percentage of carbon during the BOS process



2 Changes in the percentages of silicon, manganese and phosphorus during the BOS process



ACTIVITIES: NOTES AND ANSWERS TO QUESTIONS SS

3 Changes in the percentage of sulphur during the BOS process



a Carbon: The percentage falls rapidly during the oxygen blow (stages $B \rightarrow C$) since it is removed as carbon monoxide. It rises again after tapping as more is added to achieve the required specification.

Silicon, manganese and phosphorus: The percentage of all three elements falls during the oxygen blow as their oxides form a slag. Extra silicon and manganese are added after tapping.

Sulphur: Most is removed by combination with magnesium (stage $A \rightarrow B$). The percentage of sulphur in the molten metal increases slightly between stages $B \rightarrow C$ because of sulphur from the added scrap steel. It is then reduced even further (stages $D \rightarrow E$) probably by treatment with calcium after tapping.



- **b** The impurities in the molten iron from the blast furnace lower the freezing point below 1333 °C.
- **c** The underlying tendency is for the temperature to fall as energy is lost from the molten metal to the surroundings. The oxidation reactions of elements during the oxygen blow are highly exothermic and lead to a net increase in temperature between stages B and C.

Part 2: Making a flow diagram

The flow diagram for the BOS process might look something like this:



SS2.3 Getting the 'beat balance' right (optional extension)

This is a complex calculation involving the use of amount of substance, enthalpy changes and specific heating capacities. It might well suit able students who have time to tackle an extra exercise.

Part 1: The total energy given out by the oxidation reactions

u la					
Oxidised element	Fe	С	Si	Mn	Р
Percentage of element in molten metal charged to converter (Stage B)	-	4.42	0.57	0.41	0.085
Mass of element charged to converter/tonnes (total mass = 278 tonnes)	_	12.29	1.58	1.14	0.236
Percentage of element in molten metal at tapping (Stage C)	-	0.04	0.003	0.13	0.015
Mass of element at tapping/tonnes (total mass = 303 tonnes)	-	0.12	0.009	0.39	0.045
Mass of element oxidised/tonnes	8.5*	12.2	1.57	0.75	0.19
Amount of element oxidised/10 ⁶ mol	0.15	1.02	0.056	0.014	0.006
Molar enthalpy change/kJ mol ⁻¹	-350	-133	-745	-399	-600
Enthalpy change in converter/10 ⁶ kJ	-52.5	-135.7	-41.8	-5.6	-3.6

* Estimated from iron oxide in slag.

Total enthalpy change in the converter as a result of the b oxidation reactions = -239×10^6 kJ

Part 2: How much scrap steel is needed?

- Total energy absorbed by lime, calcined dolomite, с oxygen gas and molten iron
 - $= (18.4 \times 10^{6} \text{ kJ}) + (16.5 \times 10^{6} \text{ kJ}) + (20.8 \times 10^{6} \text{ kJ}) +$ $(86.3 \times 10^6 \text{ kJ})$
 - $= 142 \times 10^{6} \text{ kJ}$

Using the 'heat balance' equation given in the activity:

Energy given out by the oxidation reactions

- $= 239 \times 10^{6} \text{ kJ}$
- = $(142 \times 10^{6} \text{ kJ})$ + (energy absorbed by scrap steel) $+ (25 \times 10^{6} \text{ kJ})$

Energy absorbed by scrap steel = 72×10^6 kJ

- = mass scrap steel × specific heating capacity × temperature rise
- = mass scrap steel × $(0.83 \times 10^3 \text{ kJ t}^{-1} \text{ K}^{-1}) \times (1718 \text{ K})$
- \therefore Mass scrap steel = 50.5 t

(The data from a cast of steel from the British Steel Works at Scunthorpe are used as the basis of a more extensive calculation in SATIS 16-19 Unit 40 'Steel' David Whittaker and Derek Denby, Association for Science Education (1990).)

SS2.4 How much aluminium do we need to add? (optional extension)

This is a calculation for students who need practice with handling amounts of substance.

- Mass oxygen = $\frac{0.104 \times (303 \text{ t})}{100} = 0.315 \text{ t} (= 0.315 \times 10^{6} \text{g})$
- Amount of $O_2 = \frac{0.315 \times 10^6 \text{g}}{32 \text{ g mol}^{-1}} = 9844 \text{ mol}$ b
- $4Al + 3O_2 \rightarrow 2Al_2O_3$

d 9844 mol O₂ react with
$$\frac{4 \times (9844 \text{ mol})}{3} = 13 \text{ 130 mol Al}$$

Mass Al needed = 354.5 kg e

f Additional Al required =
$$\frac{0.039 \times (303 \text{ t})}{100} = 0.1182 \text{ t}$$

$$= 118.2 \,\mathrm{kg}$$

Total mass Al added = (354.5 kg) + (118.2 kg) = 472.7 kgg

h Number of ingots
$$=\frac{472.7 \text{ kg}}{20 \text{ kg}} = 24$$

i 28 ingots were actually added because some aluminium is lost by burning in air to form aluminium oxide. This will inevitably occur when the ingots are thrown into the molten metal.

SS2.5 Which is the right steel for the job? (optional extension)

Steel use	D	С	F	Е	В	Α	Η	G
Specification No.	1	2	3	4	5	6	7	8

Steels 2 and 5 have high chromium contents which suggests they are stainless steels. Steel 5 has relatively high nickel and molybdenum contents, but is low in sulphur. This would make it suitable for a severe marine environment, eg for use on an oil rig. Steel 2 has a higher carbon content than steel 5. This is consistent with the stronger material required for a surgeon's knife.

Steel 8 is a low-carbon steel. It contains relatively high amounts of lead and sulphur. This would be expected in a freecutting steel suitable for the fine machining required in the making of a spindle for a galvanometer.

Steel 3 is a low-carbon steel. It has very low phosphorus, sulphur and hydrogen contents which would make it suitable for off-shore gas pipe lines.

Steel 4 contains appreciable amounts of tungsten and molybdenum. It has the highest carbon content of the steels. It will be a hard steel, resistant to abrasion and suitable for a high speed drill tip.

Steel 6 has a very low carbon and aluminium content. This will make it malleable and ductile, so that it can be drawn into a fine wire needed in the manufacture of paper clips.

Steel 7 has a relatively high carbon content and contains significant amounts of chromium and nickel. It will be tough and hard wearing and suitable for making a ring spanner.

SS3.1 A simple redox reaction

Safety note Information about hazardous chemicals is given on the activity sheet.

- a Copper
- $Cu^{2+}(aq)$. The solution becomes paler so we know that b the concentration of $Cu^{2+}(aq)$ has fallen.
- **c** $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$ $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}; Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$
- **d** The reaction is exothermic.
- e No.

SS3.2 Simple electrochemical cells

Safety note Information about hazardous chemicals is given on the activity sheet.

The iron(II) sulphate solution must be freshly made up. You may prefer to replace the iron half-cell with an alternative such as a nickel half-cell.

Also, the half-cells can be made up in small jars using microscope slide sized pieces of metal. This gives a more stable arrangement.

- Students should be able to construct a potential a difference chart and see the links between the different voltages measured.
- **b** This will depend on the actual data they obtain, but should be 0.46V with the silver positive.

SS3.3 More electrochemical cells

Safety note Information about hazardous chemicals is given on the activity sheet.

- a Hydrogen
- **b** and **c** With care, and clean graphite electrodes, students should obtain values that are very close to standard electrode potentials.

SS3.4 How does steel rust?

Safety note Phenolphthalein indicator solution is very flammable. Full information about other hazardous chemicals is given on the activity sheet.

Advance preparation

'Ferroxyl' indicator: It is best to use a freshly prepared solution. Dissolve 10 g of sodium chloride and 1 g of potassium hexacyanoferrate(III) (**CARE** Harmful) in distilled water. Add 10 cm³ of Phenolphthalein solution (0.1% in ethanol) (**CARE** Very flammable) and make up to 500 cm³ with distilled water.

Ferroxyl' indicator in agar (optional): Sprinkle 6 g agar over 50 cm³ cold water and stir. Pour in boiling water to make the volume up to 500 cm³. Boil for 1–2 minutes. Add 10 g of sodium chloride and 1 g of potassium hexacyanoferrate(III) as above. Allow to cool a little and then add 10 cm³ of Phenolphthalein solution.

Experiment 1

This demonstrates the reaction of $Fe^{2+}(aq)$ ions with $OH^{-}(aq)$ ions, and the air oxidation of iron(II) to iron(III).

- **a** $\operatorname{Fe}(s) + 2\operatorname{H}^+(\operatorname{aq}) \rightarrow \operatorname{Fe}^{2+}(\operatorname{aq}) + \operatorname{H}_2(g)$
- **b** Dark green precipitate of iron(II) hydroxide. $Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_{2}(s)$
- **c** The dark green precipitate turns to an orange-brown solid. In air, iron(II) hydroxide is oxidised to iron(III) hydroxide.

Half-equation: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^{-}$

Experiment 2

This demonstrates the use of an $Fe^{2+}(aq)/Fe(s)$ half-cell in an electrochemical cell.

d $E_{\text{cell}} = 0.78 \text{ V}$ The Cu²⁺(aq)/Cu(s) half-cell has the more positive electrode potential.

e $\operatorname{Fe}(s) \rightarrow \operatorname{Fe}^{2+}(\operatorname{aq}) + 2e^{-}$ $\operatorname{Cu}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Cu}(s)$

Electrons flow in the external circuit from the iron halfcell to the copper half-cell. Oxidation takes place in the iron half-cell.

Experiment 3

Nail	Observations			
A	Indicator turns blue at head and point of nail but turns pink around middle section			
В	Indicator turns blue around the nail and pink around the copper			
С	Indicator turns pink around the nail. A white precipitate forms around the zinc			

f Nail A The deformation of the metal at the head and point during manufacture of the nail makes the iron more easily oxidised in these regions.

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$$

$$\frac{1}{2}O_{2}(aq) + H_{2}O(l) + 2e^{-} \rightarrow 2OH^{-}(aq)$$

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g Nail B corrodes more rapidly than nail A as an electrochemical cell is set up. Iron is the oxidation site, resulting in iron being oxidised to Fe²⁺(aq). Copper is

the reduction site, resulting in dissolved oxygen being reduced to OH⁻(aq).

Experiment 4

The central area of the drop turns blue. The outer edges turn pink. (It may also be possible to see a ring of rust forming between the two areas.)

i Reduction of dissolved oxygen occurs at the edges of the drop, where there is a plentiful supply of oxygen. Oxidation of iron occurs in the centre, where there is less oxygen.

Summary

The following mechanism for the rusting of iron should emerge:

- Points on the surface of iron in contact with water and oxygen become the electrodes in an electrochemical cell. In one half-cell, iron is oxidised to Fe²⁺(aq). In the other, dissolved oxygen is reduced to OH⁻(aq).
- These ions diffuse away from the surface of the iron and form a precipitate of iron(II) hydroxide. This is further oxidised by air to hydrated iron(III) oxide (rust).
- The reduction of dissolved oxygen tends to occur at oxygen-rich sites, while the oxidation of iron is favoured at oxygen-deficient sites.
- Zinc protects iron from rusting by forming an electrochemical cell system in which zinc is oxidised in preference to the iron.

Answers to the additional questions

j Fe²⁺ ions form a deep blue precipitate (known as *Turnbull's blue*) with potassium hexacyanoferrate(III). The reaction is used as a test for the presence of Fe²⁺ ions.

Phenolphthalein is an acid–base indicator. It is colourless in acid and pink in alkaline solution.

- **k** Magnesium or aluminium both have E^{\bullet} values more negative than iron and would oxidise in preference to iron.
- An electrochemical cell would be set up. Iron would be the oxidation site and copper the reduction site. Corrosion of the iron would be accelerated as a result.
- **m** The iron sunk into the sea bed will be cut off from supplies of dissolved oxygen in the seawater. An electrochemical cell will be set up and iron will be oxidised on the surface of the sunken areas.

SS5.1 Investigating the oxidation states of vanadium

Safety note Information about hazardous chemicals is given on the activity sheet.

The reduction of vanadium(V) with zinc can be carried out with either zinc powder or granulated zinc. The colour changes take place more slowly with granulated zinc and are easier to see, but the final colour change to violet can be very slow.

Step-by-step reduction of vanadium(V)

a As the vanadium(V) solution is shaken with the zinc, the zinc fizzes and the yellow solution turns progressively green, blue, green and finally violet. It may be necessary to warm the flask, even when using zinc dust, to obtain the final violet colour.

(*Note* The first green colour seen is a mixture of the original vanadium(V) solution and a solution of vanadium(IV).)

b	lon	Name	Oxidation state	Colour
	V02+	dioxovanadium(V)	+5	yellow
	V0 ²⁺	oxovanadium(IV)	+4	blue
	V ³⁺	vanadium(III)	+3	green
	V ²⁺	vanadium(II)	+2	violet

c The standard electrode potentials for the reduction of VO_2^+ to VO^{2+} , VO^{2+} to V^{3+} and V^{3+} to V^{2+} are all more positive than that for the $Zn^{2+}(aq)/Zn(s)$ half-cell. Therefore, the zinc half-cell with supply electrons to all three vanadium half-cells will supply electrons to all three vanadium half-cells. If excess zinc is present, a solution of vanadium(V) will be reduced to a solution containing vanadium(II).

Oxidation of vanadium(II)

d The violet solution turns progressively green, blue, (green), yellow and finally pink when excess MnO_4^- ions are present. The standard electrode potential for the reduction of MnO_4^- ions ($E^{\circ} = +1.51$ V):

 $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ is more positive than the electrode potentials for the reduction of VO_2^+ to VO^{2+} , VO^{2+} to V^{3+} and V^{3+} to V^{2+} . Thus, the three vanadium half-cells will each supply electrons to the $MnO_4^-(aq)/Mn^{2+}(aq)$ half-cell. If excess KMnO₄ is present, a solution of vanadium(II) will be oxidised to a solution containing vanadium(V).

Other redox reactions

e See SS5.1 Results table below.

Electrode potentials show that both $Fe^{2+}(aq)$ ions (in reaction **6**) and I⁻(aq) ions (in reaction **7**) can reduce vanadium(V) to vanadium(IV), but no further. The outcomes of these reactions are as predicted.

In reaction **8**, electrode potentials predict that $SO_2(aq)$ can reduce vanadium(V) to vanadium(III). The $SO_2(aq)$ would be oxidised to $SO_4^{2-}(aq)$. However, the reaction converting $SO_2(aq)$ to $SO_4^{2-}(aq)$ is slow, and so, for kinetic reasons, the reaction stops at $S_2O_6^{2-}(aq)$, and a blue solution of $VO^{2+}(aq)$ is formed.

SS5.2 How do transition metal ions act as catalysts?

Safety note Information about hazardous chemicals is given on the activity sheet.

When cobalt chloride solution is added to the mixture, there is first an induction period when nothing appears to happen. Then the mixture darkens and the temperature rises sharply. There is vigorous effervescence and the solution turns dark green. The effervescence stops as the solution becomes pink again and the temperature starts to fall. (The gas given off is a mixture of carbon dioxide from the redox reaction, and oxygen from the decomposition of hydrogen peroxide, which is also catalysed by cobalt ions.) The length of the induction period decreases with increasing concentrations of reactants and catalyst and with increasing temperature. You can vary these if necessary.

- **a** Colourless solution formed. No reaction takes place.
- **b** Pink
- **c** A complex of cobalt(III) ions with 2,3dihydroxybutanedioate ions.
- **d** The hydrogen peroxide oxidises aqueous cobalt(II) ions to cobalt(III) ions, which are stabilised by complexing

	Substances mixed	Predicted products	Predicted colour	Observation	Summary of reaction
6	$VO_2^+(aq) + Fe^{2+}(aq)$	VO ²⁺ (aq) and Fe ³⁺ (aq) blue yellow	green	green solution as predicted	$VO_2^{(+5)} \rightarrow VO^{2+}(aq)$ Fe ²⁺ (aq) → Fe ³⁺ (aq)
7	VO ₂ ⁺ (aq) + I⁻(aq) Then add thiosulphate	VO ²⁺ (aq) and I ₂ (aq) blue brown (thiosulphate reduces I ₂ to colourless I [−] ions)	brown (blue after addition thiosulphate)	as predicted	$VO_2^{(+5)} \rightarrow VO^{2+}(aq)$ $VO_2^{+}(aq) \rightarrow VO^{2+}(aq)$ $I^{-}(aq) \rightarrow I_2(aq)$
8	VO ₂ ⁺ (aq) + SO ₂ (aq) Then add vanadium(II)	V ³⁺ (aq) and SO ₄ ^{2–} (aq) green colourless (no reaction with V ²⁺ (aq))	green dark blue after addition of V ²⁺ (aq)	blue* green after addition of V ²⁺ (aq)	

* or blue-green if excess $VO^{2+}(aq)$ present. A greenish colour may also appear if too much sulphite is added. The $S_2O_6^{-2-}(aq)$ ion decomposes in acid solution to give sulphur. Filtering the greenish mixture gives a blue solution. SS5.1 Results table



with the 2,3-dihydroxybutanoate ions to form a dark green complex.

- The 2,3-dihydroxybutanoate ions are oxidised more e readily when complexed. (There is vigorous evolution of carbon dioxide accompanying the formation of the green colour.) When they have all reacted, the cobalt(III) is no longer stabilised and is reduced by water to cobalt(II).
- f Cooling slows down the redox reaction in **e**.
- The suggested mechanism should involve the oxidation g of cobalt(II) ions with hydrogen peroxide and formation of a reactive intermediate complex ion between cobalt(III) ions and 2,3-dihydroxybutanedioate ions. This complex then reacts to form the products and regenerate cobalt(II) ions.
- h Homogeneous catalysts. The catalysts and reactants are both in the same phase (both in aqueous solution). See summary table below.
- The ability to change oxidation state and the ability to i form complexes.



Progress of reaction

k A catalyst speeds up a reaction by providing an alternative route with a lower activation enthalpy. The catalyst takes part in the reaction by forming a reactive intermediate, but is re-formed at the end of the reaction.

SS5.3 Looking at some transition metal complexes

Safety note Information about hazardous chemicals is given on the activity sheet.

Part 1: Some complexes of nickel(II) ions

- Dark green; ligand Cl⁻; coordination number 4
- Light green; ligand H_2O ; $[Ni(H_2O)_6]^{2+}$ b
- $[\text{NiCl}_4]^{2-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow [\text{Ni}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq})$ с
- Nickel(II) hydroxide Ni(OH)₂ d $[\operatorname{Ni}(\operatorname{H}_{2}\operatorname{O})_{6}]^{2+}(\operatorname{aq}) + 2\operatorname{OH}^{-}(\operatorname{aq}) \rightarrow \operatorname{Ni}(\operatorname{OH})_{2}(s) + 6\operatorname{H}_{2}\operatorname{O}(l)$
- **e** Lilac/blue; ligand NH_3 ; $[Ni(NH_3)_6]^{2+}$ $Ni(OH)_2(s) + 6NH_3(aq) \rightarrow$

 $[Ni(NH_3)_6]^{2+}(aq) + 2OH^{-}(aq)$

f Blue

 $[\operatorname{Ni}(\operatorname{NH}_3)_6]^{2+}(\operatorname{aq}) + \operatorname{edta}^{4-}(\operatorname{aq}) \rightarrow [\operatorname{Ni}\operatorname{edta}]^{2-}(\operatorname{aq}) + 6\operatorname{NH}_3(\operatorname{aq})$

- Yes. Edta^{4–} forms a more stable complex with nickel(II) g than ammonia, so edta⁴⁻ ligands will displace NH₃ ligands when added to a solution of $[Ni(NH_3)_6]^{2+}$ in water.
- $[Ni(CN)_4]^{2-}$ is a more stable complex than $[Ni \text{ edta}]^{2-}$. h There would be no reaction if edta⁴⁻ ions were added to a solution of $[Ni(CN)_4]^{2-}$ ions in water.

A summary of the results for Part 1 is shown in SS5.3 Table 1 Results table below.

	Procedure	Observations	Formula of nickel complex (or nickel compound) formed
1	Addition of concentrated hydrochloric acid to solid nickel(II) chloride	Green solution formed	[NiCl ₄] ^{2–}
2	Addition of an equal volume of water	Solution becomes lighter green	[Ni(H ₂ O) ₆] ²⁺
3	Addition of sodium hydroxide solution drop by drop until a precipitate just forms	Apple-green precipitate formed	[Ni(OH) ₂
4	Addition of concentrated ammonia solution	Precipitate dissolves to form a lilac/blue solution	[Ni(NH ₃) ₆] ²⁺
5	Addition of edta ^{4–} ions	A blue solution formed	[Ni edta] ^{2–}

SS5.3 Table 1 Results table

Part 2: Precipitation reactions of copper(II), iron(II) and iron(III) ions

- $i H_2O; [Cu(H_2O)_6]^{2+}$
- **j** Copper(II) hydroxide; $Cu(OH)_2$ $Cu^{2+}(aq)+2OH^{-}(aq) \rightarrow Cu(OH)_2(s)$
- **k** Deep blue $[Cu(H_2O)_2(NH_3)_4]^{2+}$
- 1 A light blue precipitate at first, followed by a clear deep blue solution.
- **m** $\operatorname{Fe}^{2+}(\operatorname{aq}) + 2\operatorname{OH}^{-}(\operatorname{aq}) \rightarrow \operatorname{Fe}(\operatorname{OH})_{2}(s)$ $\operatorname{Fe}^{3+}(\operatorname{aq}) + 3\operatorname{OH}^{-}(\operatorname{aq}) \rightarrow \operatorname{Fe}(\operatorname{OH})_{3}(s)$ (For both NaOH(aq) and NH₃(aq))

A summary of the results for Part 2 is shown in SS5.3 Table 2 Results table below.

Transition metal ion	Observations			
	When dilute sodium hydroxide solution is added	When dilute ammonia solution is added slowly		
Copper(II)	Blue precipitate $Cu^{2+}(aq) + 2OH^{-}(aq) \rightarrow Cu(OH)_{2}(s)$	Blue precipitate of $Cu(OH)_2$ which dissolves in excess dilute ammonia solution to give a deep blue solution of $[Cu(NH_3)_4]^{2+}$		
lron(II)	Dark green precipitate $Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_{2}(s)$	Dark green precipitate of Fe(OH) ₂ . No further change when excess dilute ammonia solution added		
lron(III)	Rust-coloured precipitate Fe ³⁺ (aq) + 3OH⁻(aq) → Fe(OH) ₃ (s)	Rust-coloured precipitate of Fe(OH) ₃ . No further change when excess dilute ammonia solution added		

SS5.3 Table 2 Results table