SSI.I

How much manganese is there in a paper clip?

In this activity you will design and carry out an experiment to determine how much manganese there is in a paper clip, staple, pin or other similar everyday steel object. To do this you will need to find out how to measure the concentration of a coloured substance in solution. You will find it helpful to read **Chemical Ideas 6.7** *to find out why some compounds are coloured.*

Requirements

- paper clip (or similar everyday steel object)
- wire cutters or strong scissors
- accurate balance
- 250 cm^3 beaker
- 10 cm^3 and 100 cm^3 measuring cylinders
- nitric(V) acid, 2.0 mol dm^{-3} (100 cm^3)
- phosphoric(V) acid (10 cm^3)
- potassium iodate(VII) (periodate) solution (5 g KIO$_4$ dissolved in 100 cm^3 of 2.0 mol dm^{-3} HNO$_3$) (10 cm^3)
- Bunsen burner, tripod and gauze
- 100 cm^3 volumetric flask
- small funnel
- colorimeter with appropriate filter
- matched thin-walled (soda) test-tubes for use with colorimeter (2)
- solid potassium manganate(VII)
- dilute sulphuric acid, 1.0 mol dm^{-3}
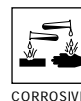- additional glassware as required
- protective gloves

CARE Potassium manganate(VII) is harmful and stains the hands. Wear protective gloves.

nitric(V) acid	IRRITANT		
phosphoric(V) acid	CORROSIVE		
potassium iodate(VII)	HARMFUL	IRRITANT	OXIDISING
potassium manganate(VII)	HARMFUL	IRRITANT	OXIDISING
sulphuric acid	IRRITANT		

CARE Eye protection and gloves must be worn.

WEAR EYE PROTECTION   WEAR PROTECTIVE GLOVES

Introduction

Steels vary greatly in composition but most will contain some manganese to increase the hardness of the alloy. In this activity you will develop a procedure for estimating the amount of manganese present in a sample of steel.

You will first convert the manganese in your paper clip into a solution containing the purple manganate(VII) ion, MnO$_4^-$(aq). This is done in two stages. Nitric acid oxidises the manganese to Mn^{2+}(aq) ions. A more powerful oxidising agent, potassium iodate(VII), KIO$_4$, is then needed to complete the oxidation to manganese(VII).

In the second part of the activity you will develop a method for determining the concentration of the manganese(VII) solution.

What you do

1 Weigh accurately about 0.2 g of cut-up paper clip or some similar everyday steel item.
2 Put it into approximately 70 cm^3 of 2.0 mol dm^{-3} nitric acid (**CARE** Irritant) in a beaker. In a fume cupboard, warm but **do not boil** the acid to help the steel to dissolve. The nitric acid oxidises the manganese to Mn^{2+}(aq) ions.
3 Add about 10 cm^3 of phosphoric(V) acid (**CARE** Corrosive) to the beaker followed by about 10 cm^3 of potassium iodate(VII) solution (**CARE** Harmful and irritant. Avoid skin contact). Boil the solution carefully for 10 minutes. Allow the mixture to cool. (The phosphoric(V) acid prevents the precipitation of insoluble iron(III) salts.)
4 When the solution is cool pour it into a 100 cm^3 volumetric flask using a small funnel. It is important not to lose any of the solution. Rinse the remaining

solution from the beaker and funnel into the flask with distilled water and add further distilled water to bring the solution in the flask exactly up to the mark.

5 Stopper the flask and shake it to ensure that the solution is uniform. All the manganese which was in your 0.2 g of paper clip is now in the purple solution as the manganate(VII) ion (MnO_4^-(aq)).

Determining the concentration of a coloured solution

You now need to find out the concentration of the purple solution so that you can calculate the amount of manganese originally in the paper clip.

The concentration of a coloured solution can be found quickly and easily with a **colorimeter**.

Figure 1 shows a simplified diagram of a colorimeter. A narrow beam of light passes through the solution under test and towards a sensitive photocell. In most colorimeters it is possible to select light in the most appropriate region by turning a knob to select a particular filter or to adjust a diffraction grating.
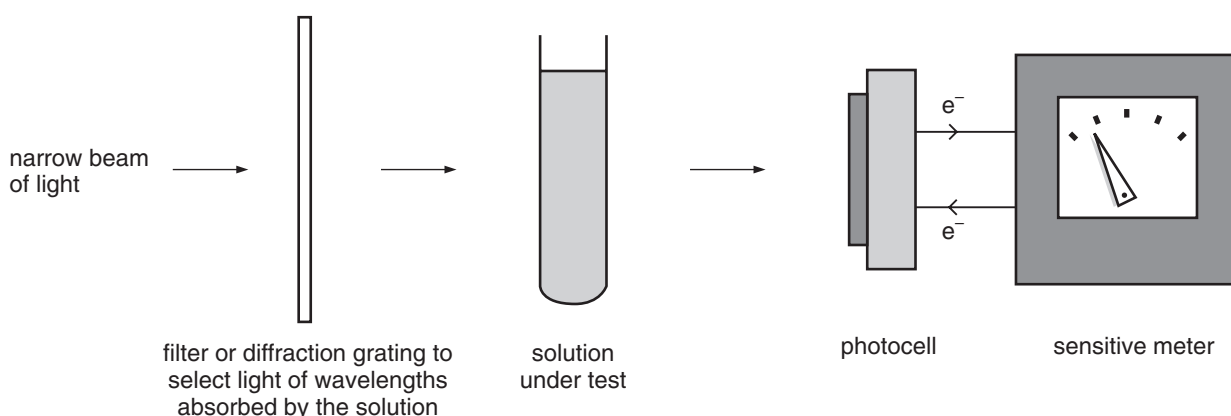

narrow beam of light

filter or diffraction grating to select light of wavelengths absorbed by the solution

solution under test

photocell   sensitive meter

Figure 1 Simplified diagram of a colorimeter

The current generated in the photocell depends on the amount of light transmitted by the solution. This in turn depends on the concentration of the coloured solution under test. Normally the meter is calibrated to show the **absorbance** of the solution, rather than the light transmitted, because the absorbance is proportional to the concentration of the coloured substance in solution:

$$\text{absorbance} \propto \text{concentration of coloured solution}$$

(You can read in **Chemical Ideas 6.7** about why some solutions are coloured.)

Designing your experiment

6 Now plan your experiment. It will be helpful to discuss your ideas in pairs or small groups.

You will need to produce a calibration graph by plotting the absorbance of potassium manganate(VII) solution (*y*-axis) against its concentration (*x*-axis). You will need about five or six points on your graph. The absorbance of the solution from the paper clip can then be measured and its concentration read off from the graph.

Most steels contain less than 2% of manganese and a typical value for the steel used in a paper clip is about 0.3%. Use these figures to calculate the maximum mass of $KMnO_4$ which could be present in 100 cm³ of solution from your paper clip. Use 1.0 mol dm⁻³ sulphuric acid (**CARE** Irritant) to dissolve the potassium manganate(VII) (**CARE** Powerful oxidiser. Harmful and irritant. Avoid skin contact).

Consider the following points:

- What range of concentrations of solution will you need to enable you to plot a calibration curve?
- How many different concentrations will you need and what should they be?
- What is the most accurate way of making up these solutions? Remember, they will be very dilute.
- What apparatus will you need?
- Which chemicals?

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7 Write an outline plan of your experiment. Prepare a **Risk Assessment** for your planned activity and a list of sources you have used in developing your plan and your Risk Assessment. Do not start until you have discussed these with your teacher.

8 Having made your plans you can now go ahead to get some results. From the results, work out the percentage of manganese in your paper clip.

9 When you have finished, write out your method in such a way that it could be used by another chemist without further help. Include your result as a guide to the figure which might be expected.

QUESTIONS

a Explain how the first stages of the procedure you used could give a *qualitative* test for manganese in steel.

b You probably made up the potassium manganate(VII) solutions for your calibration graph using some form of dilution technique. Explain how diluting solutions in this way can lead to errors in your measurements.

c Why is it necessary to use carefully matched tubes in a colorimeter?

d Calculate the percentage error for each of the measurements you have made. In view of these uncertainties and any sources of procedural errors you have identified, how many significant figures are you justified in using for the percentage of manganese in the paper clip?

e Why is a green or yellow-green filter chosen in this experiment? What general principles should be used when choosing a filter for a colorimetric investigation?

f This activity illustrates an important aspect of the chemistry of manganese which is its ability to form compounds in a variety of oxidation states. What is the oxidation number of manganese in Mn, Mn^{2+} and MnO_4^-? Explain why the conversion of Mn to MnO_4^- is an oxidation process.

g A solution of manganate(VII) is a powerful oxidising agent and is often used to titrate substances which are readily oxidised. You may have used a solution of manganate(VII) to find out the amount of iron in an iron compound in **The Elements of Life**, **Activity EL2.1**.

Explain why a similar redox titration method could not be used to find the concentration of the manganese(VII) solution from your paper clip. (Hint: Think about what other chemicals may be in your solution.)

In this activity you use a solution of potassium manganate(VII) to carry out a redox titration to investigate the oxidisable material present in spinach.

Requirements

- spinach/spinach beet (15 g) or rhubarb leaves (5 g)
- scissors
- 250 cm^3 beaker
- sulphuric acid, 1.0 mol dm^{-3} (300 cm^3)
- 100 cm^3 measuring cylinder
- Bunsen burner, tripod and gauze
- Buchner funnel and vacuum filtration apparatus
- 100 cm^3 volumetric flask
- 10 cm^3 pipette amd pipette filler
- 250 cm^3 conical flask
- 0–110 °C thermometer
- burette
- potassium manganate(VII) solution, 0.01 mol dm^{-3} (150 cm^3)
- protective gloves

sulphuric acid

IRRITANT

CARE Eye protection must be worn.

WEAR EYE PROTECTION

CARE Take care when pouring potassium manganate(VII) solution as it stains the hands. Wear protective gloves if necessary.

Introduction

Iron is an important mineral element in foods. The recommended intake for adults is 10–15 mg per day and each person contains about 4 g of iron, mainly in the haemoglobin of red blood cells. Surprisingly human beings absorb less than 10% of the iron in their diet. The reason for this is that only iron(II) ions are absorbed whereas most of the iron in foods is iron(III). Vitamin C reduces a small proportion of the iron(III) to iron(II) and ensures that it does not re-oxidise.

Spinach and spinach beet have a high iron(II) content (4 mg per 100 g) but this cannot be absorbed in the stomach because it is locked up in insoluble oxalate (ethandioate) complexes.

This experiment investigates the amount of iron(II) and oxalate present in spinach by means of a redox titration.

What you do

1 Weigh approximately 15 g of spinach/spinach beet. (If using rhubarb leaf substitute, only use 5 g and remember it is poisonous if eaten due to the high oxalate content.)
2 Using scissors, cut the leaves into small pieces and place in a 250 cm^3 beaker. (If frozen spinach is used then simply place in the 250 cm^3 beaker.)
3 Using a measuring cylinder, add 50 cm^3 1.0 mol dm^{-3} sulphuric acid (**CARE** Irritant) and boil the mixture gently for 5 minutes.
4 Allow the mixture to cool a little and filter it, using a Buchner funnel and vacuum filtration. Wash the residue in the funnel once with a little distilled water and collect all the filtrate.
5 Pour all the filtrate and washings into a 100 cm^3 volumetric flask. Make up to 100 cm^3 with 1.0 mol dm^{-3} sulphuric acid. Stopper the flask and shake it well.
6 Fill a burette with potassium manganate(VII) solution. (**CARE** Stains the hands. Avoid skin contact and wear protective gloves if necessary.)
7 Using a pipette, transfer 10 cm^3 of the spinach extract solution to a 250 cm^3 conical flask and add 50 cm^3 of 1.0 mol dm^{-3} sulphuric acid using a measuring cylinder. Heat the mixture to 60 °C.
8 Titrate the solution in the conical flask with 0.01 mol dm^{-3} potassium manganate(VII) solution from the burette until the pink colour persists for 30 seconds.

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9 Repeat until there are three titration values (titres) within $0.1\,cm^3$ of each other. Record your results.

Record your results

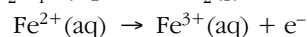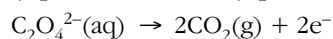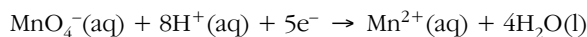Mass of spinach =   g

	Rough	1	2	3	4
Final burette reading / cm^3					
Initial burette reading / cm^3					
Titration value (titre) / cm^3					

Average titre = cm^3

Using your results

The formula of iron(II) oxalate is $Fe_2(C_2O_4)_2$ (which is more correctly written as $Fe[Fe(C_2O_4)_2(H_2O)_2]$).

Both the $Fe^{2+}(aq)$ ions and the $C_2O_4^{2-}(aq)$ ions react with potassium manganate(VII). The half equations for these reactions are:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$
$$C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$$
$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

When these half-equations are combined to give an overall equation for the reaction of MnO_4^- ions with $Fe_2(C_2O_4)_2$, it can be shown that 6 moles of $MnO_4^-(aq)$ react with 5 moles of $Fe_2(C_2O_4)_2$.

10 Using your average titration value work out the number of moles of potassium manganate(VII) used.
11 Assuming that the potassium manganate(VII) has reacted only with iron(II) oxalate, how many moles of $Fe_2(C_2O_4)_2$ would be present in the $10\,cm^3$ sample of extract?
12 What would be the total number of moles of $Fe_2(C_2O_4)_2$ in the $100\,cm^3$ sample of extract?
13 What mass of $Fe_2(C_2O_4)_2$ would be in the sample of spinach?
14 What would be the $Fe_2(C_2O_4)_2$ content of spinach in g per 100 g?
15 Comment on the value you obtain in **14** in the light of the information given in the introduction.

QUESTIONS

a At the endpoint of the titration the pink colour persists for about 30 seconds. What is the pink colour due to?

b Suggest why the spinach extract solution has to be heated to 60 °C for the titration.

Why is blast furnace iron so impure?

This activity will help you to understand why the iron produced in a blast furnace is so impure.

Blast furnace iron is the starting material for making steel. To answer the questions below you may have to refer back to your earlier work on iron or look up the blast furnace in a textbook. Use this activity to make *brief* summary notes about how iron is produced in a blast furnace.

QUESTIONS

a What raw materials are fed into a blast furnace?

b Explain why the conversion of iron ore to iron is a reduction. Name the main reducing agent.

c Summarise the chemical reactions which take place, using a series of chemical equations.

d The iron produced contains 3–5% carbon. Where has this carbon come from?

e What is the origin of the silicon impurity present? Much silicon has already been separated out from the iron inside the blast furnace. Explain how this was done.

f Suggest likely origins for the sulphur, phosphorus and manganese impurities in the iron produced.

A2 LEVEL

In this activity you will investigate the changes in composition and temperature as a batch of steel is made by the BOS process. It will give you an opportunity to practise using a computer spreadsheet program to handle data, draw bar charts and plot graphs. The second part of this activity will also give you an overview of how steel is made.

Part 1: Plotting the changes

The Corus (formerly British Steel) Works at Scunthorpe produce some steel suitable for making the carbon dioxide cylinders used in Sodastream fizzy drinks makers. You may have watched a batch being produced on the **The Steel Story** video.

The cylinders are pressed to shape from circular discs cut out of thin steel plate. The steel must be ductile so that it can be moulded without developing cracks, but strong enough to hold the gas safely at 28 atmospheres pressure. You are going to investigate the changes in composition and temperature which happened while a batch of this steel was being made.

The best way to do this activity is to use a computer with the facility to draw bar charts and plot graphs from stored data. This is a much easier and quicker way of handling data than by manual plotting.

You can speed things up by working in groups, so that each group plots one chart or graph. At the end pool your results.

Changes in composition

Table 1 shows the percentages of the elements carbon, silicon, manganese, phosphorus and sulphur in the molten metal at five different stages (labelled A to E) during the BOS process.

1 Draw a bar chart showing how the percentage of carbon changes during the process. (The five stages A to E should be on the *x*-axis; the percentage of carbon should be on the *y*-axis.)
2 Using a new set of axes, plot a similar chart showing how the percentages of silicon, manganese and phosphorus change. Plot the values for all three elements on the same chart.
3 Plot a chart on a third set of axes showing how the percentage of sulphur changes.

   a Write a short explanation of the changes in the percentages of the five elements shown by your charts.

Table 1 Analysis data for a cast of steel for Sodastream from the Scunthorpe Works of Corus.

	Temp/°C	%C	%Si	%Mn	%P	%S
Customer's specification		0.34–0.39	0.15–0.25	1.40–1.50	<0.02	<0.003
Target at tapping*	1699	0.04	0.00	0.1	0.015	0.005
Stage A Molten iron received from the blast furnace	1333	4.42	0.66	0.41	0.085	0.027
Stage B After magnesium injection	1311	4.42	0.57	0.41	0.085	0.003
Stage C Molten steel at end of oxygen blow	1738	0.04	0.003	0.13	0.015	0.006
Stage D Steel after tapping, main additions and argon stir	1622	0.34	0.058	1.40	0.015	0.005
Stage E Molten steel leaving for continuous casting	1598	0.38	0.21	1.43	0.016	0.002

* Tapping: removing molten steel from the converter at the end of the oxygen blow.

Changes in temperature

4 Using the information in Table 1, plot a graph to illustrate how the temperature of the metal changes during the BOS process.

5 Draw a dotted line across your graph to show the target tapping temperature. (This is the ideal temperature for steel leaving the converter at the end of the oxygen blow.)

   b The freezing point of pure iron is 1539 °C yet the metal arriving from the blast furnace is molten at a temperature of 1333 °C. Why has it not solidified?

   c Write a short explanation of the changes in temperature shown by your graph.

Part 2: Making a flow diagram

A flow diagram is one way of summarising the stages in a complex process such as steelmaking. Flow diagrams can be helpful in picking out the main thread from a complicated text and giving you a visual picture of the overall scheme.

Starting with blast furnace iron, as shown in the incomplete diagram in Figure 1, construct your own flow diagram to show the steps involved in steelmaking. Make sure you show the steps in the right order and think about the substances which leave the process as well as the ones that are added.

You can draw the flow diagram by hand or use a computer drawing program. You may find it helpful to summarise other parts of your work in this way.
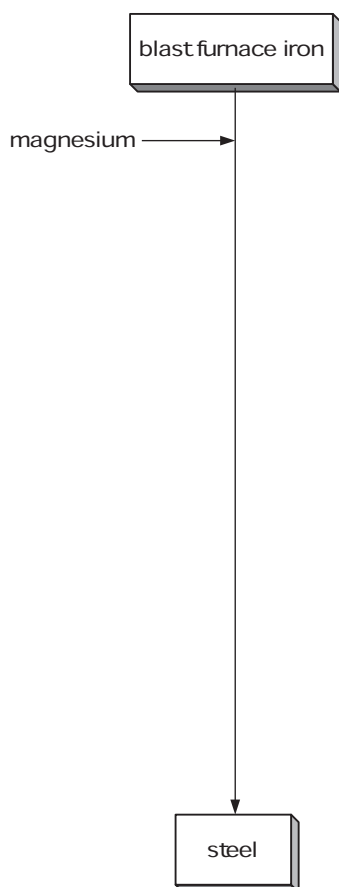

Figure 1 A flow diagram to show the production of steel from iron

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Controlling the temperature to keep it within acceptable limits is an essential part of the BOS process. It is done by adding scrap steel to the converter along with the molten iron. In this activity you will work out how much scrap would be needed for a given batch of steel to achieve its target tapping temperature.

Introduction

The energy changes which take place in the converter during the BOS process can be summarised by a 'heat balance' equation as shown below:

Energy given out by the oxidation reactions of Fe, C, Si, Mn and P	=	Energy used in raising the temperature of the converter contents (lime, calcined dolomite, oxygen, iron and scrap steel)	+	Energy used in heating the surroundings

At the steelworks, all these energy changes are estimated using a computer model. It calculates the amount of scrap steel, lime and calcined dolomite (a mixture of calcium and magnesium oxides made by heating dolomite) and the duration of the oxygen blow required to give the chosen specification and the final temperature of the steel.

In this activity you will carry out this type of calculation for yourself. You are going to work out first how much energy was generated by the oxidation reactions when a cast of steel for Sodastream was made at the Corus Works at Scunthorpe. Then, you will go on to estimate the amount of scrap steel needed in the converter so that the temperature does not rise above the target tapping temperature. You will need to consult Table 1 in **Activity SS2.2** which gives information about this batch of steel.

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

a Calculate the enthalpy change for each of the exothermic reactions taking place in the converter. Do this by filling in Table 1 below using information from Table 1 in **Activity SS2.2**. The values for carbon have already been filled in for you.

You will need to watch the units in your calculation carefully. The masses in the converter are given in tonnes (1 tonne = 1000 kg = 1×10^6 g). The molar enthalpy changes give the enthalpy change when 1 mole of each element is oxidised; for carbon the mass of 1 mole of atoms is 12.0 g.

(A_r: Fe, 56; C, 12; Si, 28; Mn, 55; P, 31)

Table 1 Exothermic changes in the BOS converter

Oxidised element	Fe	C	Si	Mn	P
Percentage of element in molten metal charged to converter (Stage B)	–	4.42			
Mass of element charged to converter/tonnes (total mass = 278 tonnes)	–	12.29			
Percentage of element in molten metal at tapping (Stage C)	–	0.04			
Mass of element at tapping/tonnes (total mass = 303 tonnes)	–	0.12			
Mass of element oxidised/tonnes	8.5*	12.2			
Amount of element oxidised/10^6 mol		1.02			
Molar enthalpy change/kJ mol^{-1}	–350	–133	–745	–399	–600
Enthalpy change in converter/10^6 kJ		–135.7			

* Estimated from iron oxide in slag

b Now calculate the *total enthalpy change* in the converter as a result of these oxidation reactions.

Part 2: How much scrap steel is needed?

This involves a lengthy calculation: we have done some of it for you, and you will do only the last part.

Look back at the 'heat balance' equation on the previous page. Some of the energy given out by the oxidation reactions is lost from the converter to the surroundings through normal cooling. It can be estimated that approximately 25×10^6 kJ were lost by radiation and convection in this way.

The rest of the energy released by the oxidation reactions is used to raise the temperature of the converter contents. We can calculate how much energy is required to raise each of the contents of the converter from their initial temperatures to the final temperature if we know how much of each substance was added and its specific heating capacity. The results of such calculations are shown in Table 2.

Material	Quantity added to converter	Energy absorbed /10^6 kJ
Lime	11.9 tonnes	18.4
Calcined dolomite	9.49 tonnes	16.5
Oxygen gas	$16.8 \times 10^3 \, m^3$	20.8
Molten iron	278 tonnes	86.3
Scrap steel	?	?

Table 2 Energy absorbed in heating up the contents of the converter

c   Using the information above, calculate how much scrap steel was needed in order to achieve the tapping temperature of 1738 °C. Assume that the steel added was at 20 °C and that the specific heating capacity of steel is 0.83×10^3 kJ t^{-1} K^{-1}. (This value has been averaged out over the temperature range and allows for the enthalpy change of fusion on melting. It gives the amount of energy which must be supplied to raise the temperature of 1 tonne of steel by 1 K.)

The energy absorbed by the steel is related to the rise in temperature in the following way:

energy absorbed = mass × specific heating capacity × temperature rise

How much aluminium do we need to add? (Optional extension)

This activity is about the role of aluminium in steelmaking. Aluminium is used to remove oxygen dissolved in the steel but is also one of the elements added to modify the properties of the metal. You will calculate the amount of aluminium that must be added to a batch of steel to perform both these functions.

You will again be using information about the steel cast which you met in **Activities SS2.2** and **SS2.3**.

The total mass of steel tapped from the converter at the end of the oxygen blow was 303 tonnes.

Work through the following questions to calculate how much aluminium must be added to remove dissolved oxygen and meet the customer's specification for aluminium content.

You will need to think carefully about units of mass during your calculation. The mass of steel in the converter is given in tonnes, while the aluminium ingots are weighed in kilograms. The molar masses of oxygen and aluminium are in $g\,mol^{-1}$.

(1 tonne $= 1000\,kg = 1 \times 10^6\,g$) ($A_r$: O, 16; A1, 27)

_____ **QUESTIONS** _____

a Analysis of the steel tapped from the converter showed that it contained 0.104% oxygen. Calculate the mass of this oxygen in tonnes.

b Convert this mass of oxygen to the amount in moles of O_2.

c Write a balanced equation for the reaction between aluminium and oxygen.

d Calculate the amount in moles of aluminium needed to react with this dissolved oxygen.

e What is the mass of aluminium needed, in kilograms?

f Assume all of this aluminium is lost as a slag. The customer's specification for the batch of steel requires 0.039% aluminium. Calculate the additional mass of aluminium, in kilograms, which must be added to achieve this.

g Work out the *total* mass of aluminium added to the steel.

h The aluminium is thrown into the molten steel as 20 kilogram ingots. How many ingots should be used?

i In fact, 28 ingots of aluminium were added to this cast to achieve the specification. Suggest why this is different from the figure you have just worked out.

SS2.5

Which is the right steel for the job? (Optional extension)

This activity illustrates how the properties and eventual use of a steel relate to its composition.

Introduction

An army tank and a kitchen sink are each made from steel. The different uses demand quite different properties from the metal, however. One of the major factors leading to different properties is the composition of the steel.

What you do

Use the **Information Sheet** (*Some elements and their effects on the properties of steel*) to match the eight steel uses (**A–H**) to the specifications numbered **1–8** in Table 1.

The first one has been done for you to show you the idea: the steel with specification number **1** would be suitable for use D, the CO_2 cylinder for a fizzy-drinks maker. The steel must be capable of being moulded into shape without developing cracks, but must be strong enough to hold the gas safely at high pressure. So a medium-carbon steel is used with aluminium and manganese added for toughness and good moulding properties. Low sulphur, phosphorus and nitrogen reduce its tendency to crack.

Now match the most suitable composition to each of the remaining steel applications. Briefly explain the reasons for your answers.

Steel uses

A   A paper clip (mild steel which can be drawn to form a wire)
B   Stainless steel for severe marine environments, such as in living quarters on oil rigs
C   Stainless steel for a surgeon's knife
D   Sodastream CO_2 cylinder
E   A high-speed drill tip
F   An off-shore gas pipe
G   A finely-machined spindle for a galvanometer
H   A ring spanner

Steel specification	1	2	3	4	5	6	7	8
C	0.350	0.110	0.100	0.750	0.025	0.043	0.500	0.070
Si	0.200	0.350	0.400	0.400	0.350	0.042	0.300	0.005
Mn	1.400	0.650	1.500	0.400	1.700	0.252	1.000	1.300
P	0.018	0.030	0.009	0.350	0.040	0.013	0.035	0.060
S	0.003	0.010	0.001	0.350	0.007	0.014	0.035	0.350
Cr	0.20	12.50	0.03	4.00	17.20	0.02	1.00	0.03
V	0.15	0.15	0.15	1.20	0.20	0.15	0.15	0.15
Mo	0.002	0.30	0.002	<0.7	2.65	0.002	0.08	0.002
W	<0.001	0.10	<0.001	18.00	0.20	<0.001	<0.001	<0.001
Nb	0.001	0.10	0.03	0.001	0.10	0.001	0.001	0.001
Cu	>0.20	0.500	0.150	<0.2	0.500	0.028	0.350	0.02
Ni	0.20	0.350	0.150	<0.4	11.70	0.025	0.400	0.02
Pb	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.2500
Te	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.02
N	0.0008	0.0400	0.0060	0.0400	0.0350	0.0049	0.0400	0.0050
H (ppm)	10	10	<2	10	10	10	10	10
Al	0.050	0.02	0.03	0.020	0.02	0.002	0.02	0.02
Steel use	D							

Table 1 Specifications for eight different steels: the figures give the percentage of each element in the steel

A2 LEVEL

Some help if you need it

- For each of the steel uses **A**–**H** make a list of the important properties the steel should possess, as well as properties it need not possess.

- Now read the **Information Sheet** carefully and jot down under each steel use the key elements to look for in the steel specification (eg high Cr or low S).

- Look through the steel specifications in Table 1 and identify the two stainless steels. Examine carefully the specifications for these two steels and use the **Information Sheet** to decide on the most appropriate use for each.

- Carbon content is a good initial indicator to the eventual use of the steel. Divide the remaining steel specifications into relatively high- and low-carbon steels. Then look for additional elements which confer specific properties, such as good machinability or resistance to wear.

Low-carbon steel	0.003–0.15% C
Medium-carbon steel	0.16–0.40% C
High-carbon steel	0.41–0.92% C

(High-carbon steels may well extend above 0.92% C in the coming years as new steels come on stream.)

Information Sheet: Some elements and their effects on the properties of steel

Nickel

Nickel promotes toughness at low temperatures and reduces the chances of brittle fractures.
Nickel is relatively inert and improves the corrosion resistance of steel. Up to 8% nickel is used in some stainless steels.

Niobium

Niobium forms an extremely hard and stable carbide. It is added to some stainless steels to increase resistance to corrosion and is also a constituent of abrasion-resistant steels and steels to be used at high temperatures.

Nitrogen

All steels contain some dissolved nitrogen from the air. Generally nitrogen is undesirable in steel because it makes the metal less ductile.

Copper

Copper is added to steel to increase corrosion resistance. It also increases strength. Scrap electrical motors are often used as the source of copper.

Aluminium

Aluminium is often added to the molten metal because it forms a fine precipitate of aluminium nitride as the steel solidifies; this limits the size of the crystals formed in the cooling metal. The resulting material can be easily shaped, yet is tough and has good impact resistance. Aluminium is added to steel for car body panels, but is kept to a minimum in steel which is to be drawn out into wire, as regions of aluminium oxide tend to cause breakages.

Carbon

Carbon is the most important alloying element in steel. By changing the carbon content a wide variety of mechanical properties can be produced:
• Metal from the blast furnace (4% C) is very brittle.
• High-carbon steel (1% C) is strong and resistant to hard wear.
• Low-carbon or mild steel (0.008% C) is less strong but easily moulded.

Chromium

Chromium makes steel resistant to corrosion. Stainless steel contains 12-25% chromium. Chromium also improves wear resistance and helps steel to retain its strength at high temperatures (used in high-speed tools).

Manganese

Manganese is the most used alloying metal in steel. Manganese improves the quality of steel by making it easier to work when hot and increasing hardness when cold. Manganese combines with residual sulphur to form small, evenly distributed sulphide crystals. It is present in all steels but is particularly important in steels used to make tools and dies.

Silicon

Silicon is added to most steels because small amounts improve the hardness and strength of the alloy.

Sulphur

Usually much care is taken by steelmakers to reduce the sulphur content of steel. Sulphur increases corrosion rate, promotes stress corrosion cracking and increases brittleness at low temperatures. The development of the off-shore and arctic oil industry has increased the demand for high-grade steels with very low sulphur content.
However, small amounts of sulphur (0.08-0.13%) make it easier to machine the metal. Steel chips break away more easily during machining if there is iron sulphide present. This reduces tool wear and the volume of turning waste.

Phosphorus

Small amounts of phosphorus severely reduce the quality of steel by reducing ductility. Ordinary steels have concentrations less than 0.04% but many steel specifications where cracking would be a very serious problem (such as in a gas pipeline) require the phosphorus concentration to be as low as 0.005%.

Vanadium

Vanadium promotes small crystal size in steels and increases the strength, hardness and wear resistance. It is an expensive addition to steel and so it is only used where the steel will experience exceptionally severe service, such as in tools and dies, structural steels for military vehicles, and rails (curves, switches and points).

Hydrogen

Steelmakers go to considerable lengths to limit the hydrogen in steel. Hydrogen is produced when any moisture comes into contact with the molten steel.
$$Fe + H_2O \rightarrow FeO + H_2$$
Atomic hydrogen in steel migrates to internal defects where it forms hydrogen gas and builds up high pressures. This can cause flaking at the surface and even fracturing in such items as pipelines.

Lead

Lead improves the machinability of steel. Small quantities are added to steel which is intricately machined into gears and shafts because it helps to cut down on wear of tools. Machine operators must take precautions to avoid lead poisoning when working with these steels.
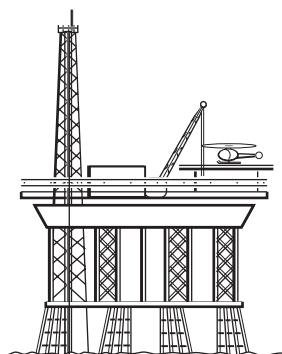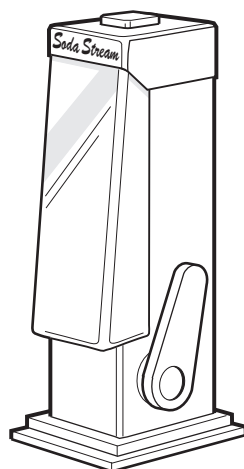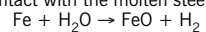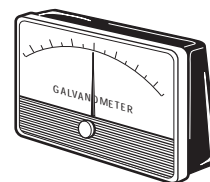
Molybdenum

Molybdenum is a valuable additive for the hardening of steel. It retards the softening of steel at high temperatures and improves the corrosion resistance of stainless steels. Molybdenum is used in steels for boilers, high-speed tools and for special stainless steels used for cladding oil-rig modules and for containers for corrosive liquids.
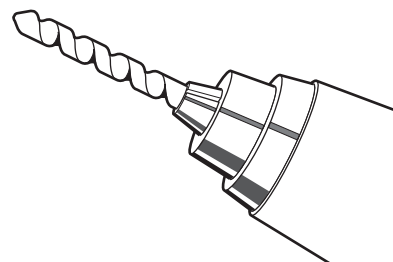
Tungsten

Tungsten is an important additive to high-speed tool steels. It forms hard carbides which have high abrasion resistance. It helps to retain high strength in steels at high temperature. It is used in fire-resistant construction steels.

Tellurium

Tellurium is added to steels to improve machinability, either alone or with lead. Fumes from tellurium compounds can be noxious and proper venting must be provided whenever additions are made – otherwise workers can develop 'tellurium breath', with a strong garlic-like odour.

In this short activity you will study one redox reaction in some detail to examine some of the general features of redox reactions. **Chemical Ideas 9.1 and 9.2** *will help you interpret the results of this experiment.*

Requirements

- test-tubes or small beakers
- copper(II) sulphate solution, $1.0 \, mol \, dm^{-3}$ ($20 \, cm^3$)
- zinc(II) sulphate solution, $1.0 \, mol \, dm^{-3}$ ($20 \, cm^3$)
- strips of zinc and copper (long enough to reach into the solutions)
- zinc powder (1 g)
- filter funnel and paper
- $0–110 \, °C$ thermometer

copper(II) sulphate HARMFUL

zinc powder FLAMMABLE

CARE Eye protection must be worn. WEAR EYE PROTECTION

What you do

1 Half-fill a test-tube with $1.0 \, mol \, dm^{-3}$ copper(II) sulphate solution (**CARE** Harmful). Note its temperature.

2 Dip a strip of zinc into the solution and leave it for a short time. Remove the zinc, examine its surface, and record the changes you observe.

3 Now add a spatula of zinc powder (**CARE** Flammable) to the test-tube of copper(II) sulphate solution. Stir, and record the maximum temperature reached.

4 Filter the mixture. Compare the appearance of the filtrate with the colour of the original copper(II) sulphate solution. Be sure to make a fair comparison.

5 Test whether copper reacts with zinc(II) sulphate solution.

QUESTIONS

a A solid coats the surface of the zinc. What do you think it is?

b What ion is responsible for the blue colour of copper(II) sulphate solution? What has happened to the concentration of this ion during the reaction?

c Write an overall equation for the reaction of zinc with copper(II) ions, and then split it into two half-reactions which show clearly that a redox reaction is involved.

d What does the temperature change tell you about the reaction?

e Does the reverse reaction happen?

This activity gives you a chance to set up a number of electrochemical cells. You will need to use your experimental skills to obtain reliable data on the cells. You then have an opportunity to develop your abilities in analysing data. You will learn about the relationship between the potential differences of different cells. **Chemical Ideas 9.2** *will help you interpret your results.*

Requirements

- leads with crocodile clips (2)
- 100 cm³ beakers (3)
- iron nail
- copper metal strip (long enough to dip into the solution in the beaker)
- zinc metal strip (long enough to dip into the solution in the beaker)
- emery paper
- distilled water
- copper(II) sulphate solution, 1.00 mol dm⁻³ (50 cm³)
- iron(II) sulphate solution, 1.00 mol dm⁻³ (50 cm³)
- zinc(II) sulphate solution, 1.00 mol dm⁻³ (50 cm³)
- filter paper strips soaked in saturated potassium nitrate(V) solution
- high-resistance voltmeter (e.g. pH/mV meter)

copper(II) sulphate ❌ HARMFUL

**CARE** Eye protection must be worn. 🥽 WEAR EYE PROTECTION

Introduction

You have probably used batteries in a number of different appliances. They are often called 'dry' cells because, for convenience, pastes rather than solutions are used in making up the cells. They are all based on redox reactions arranged to occur in two half-cells. The electricity produced is generated by a chemical reaction taking place in the cell.

In this activity you will set up a number of metal ion/metal half-cells, combine them into cells, and measure the potential differences with a high-resistance voltmeter.

What you do

1 Clean the metal strips by rubbing them with emery paper, rinsing in distilled water, and drying them.
2 Pour the copper(II) sulphate solution (**CARE** Harmful) into a beaker and place the copper metal strip into it. This forms the copper half-cell (Figure 1). You can bend the foil over the edge of the beaker and hold it in place with the crocodile clip.

copper metal

copper(II) sulphate solution
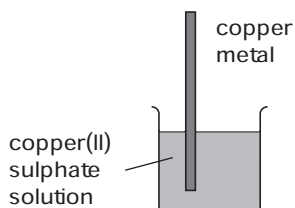
The beaker contains both copper atoms (in the metal) and copper ions (in the solution)

Figure 1 A copper half-cell, $Cu^{2+}(aq)/Cu(s)$

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3 Put the zinc(II) sulphate solution and the zinc strip in the other beaker. This is the zinc half-cell.

4 Take a strip of filter paper soaked in saturated potassium nitrate(V) solution, and use it as a salt (ion) bridge to connect the solutions in the two beakers.

5 Make sure that you know how to operate the voltmeter you will be using. Then complete the circuit by connecting the copper and zinc strips to the voltmeter as shown in Figure 2.
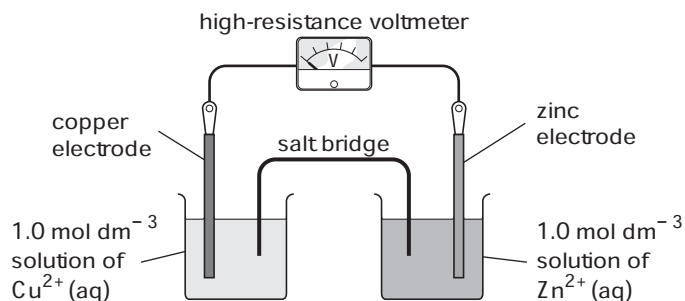

Figure 2 Arrangement for measuring the voltage of an electrochemical cell

6 Record the voltage of the zinc–copper cell, and note carefully which half-cell is positive and which negative.

7 Prepare an iron half-cell, $Fe^{2+}(aq)/Fe(s)$. Use a fresh salt bridge to connect it to a copper half-cell. Measure the voltage of the iron–copper cell.

8 Finally, measure the voltage of a zinc–iron cell.

9 If other half-cells are available you could extend your series of measurements.

10 Do not throw away the metal-ion solutions, but return them to the containers provided.

—————————————— **QUESTIONS** ——————————————

Use **Chemical Ideas 9.2** to help you interpret the results of this experiment.

a Using the data you have obtained, construct a chart showing the potential differences between the half-cells you have investigated. **Chemical Ideas 9.2**, Figure 10, shows you how to do this.

b The voltage of a silver–iron cell is 1.24 V, with the silver positive. Include this data on the chart you have constructed, and use it to calculate the voltage of a silver–copper cell.

This activity extends your experience of half-cells to ones in which both reagents are in solution. You will investigate whether these half-cells can combine to make electrochemical cells in a way similar to metal ion/metal systems. **Chemical Ideas 9.2** *will help you interpret your results.*

Requirements

- copper(II) sulphate solution, $1.00 \, mol \, dm^{-3}$ ($50 \, cm^3$)
- copper metal strip (long enough to dip into the solution in the beaker)
- emery paper
- $100 \, cm^3$ beakers (2)
- leads with crocodile clips (3)
- d.c. power supply able to give $3 \, V$
- clean graphite electrodes (2)
- filter paper strips soaked in saturated potassium nitrate(V) solution
- high-resistance voltmeter (eg pH/mV meter)
- potassium iodide solution, $1.00 \, mol \, dm^{-3}$ ($50 \, cm^3$)
- potassium bromide solution, $1.00 \, mol \, dm^{-3}$ ($50 \, cm^3$)
- potassium chloride solution, $1.00 \, mol \, dm^{-3}$ ($50 \, cm^3$)

CARE The chlorine and bromine produced in Part 1 of this activity are toxic and corrosive gases. Avoid inhaling any fumes and do not let the electrolysis run for more than 1–2 minutes.

bromine   TOXIC   CORROSIVE

chlorine   TOXIC   CORROSIVE

copper(II) sulphate   HARMFUL
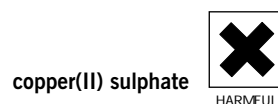
CARE Eye protection must be worn.   WEAR EYE PROTECTION

Introduction

The half-cells you have looked at so far have involved a metal and its ion. In this activity you will investigate half-cells where no metal is involved. You will investigate halogen/halide ion half-cells. You must first make these, as follows.

The halogen is generated by *electrolysis*, by passing an electric current through a solution of a metal halide. The halogen is produced at one of the graphite electrodes, covering its porous surface. The result is a half-cell consisting of the halogen (X_2) in contact with a solution of halide ions (X^-). The graphite electrode provides electrical contact and takes no part in the redox reaction.

$$X_2 + 2e^- \rightleftharpoons 2X^-$$
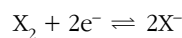
In the second part of the activity, you will connect the halogen/halide ion half-cell to a standard copper half-cell to make an electrochemical cell, and then measure its voltage.

You can use the potential difference between the two half-cells to work out the electrode potential of the halogen/halide ion half-cell.

Before you start this activity, make sure you understand what is happening in each part.

What you do

Part 1: Making the two half-cells

1 Clean the copper electrode and set up a copper half-cell. (**CARE** Copper(II) sulphate solution is harmful.)
   Now make a halogen/halide ion half-cell as described in steps **2**–**4**.
2 Start with the potassium iodide solution. Place two graphite electrodes into $50 \, cm^3$ potassium iodide solution in a beaker and connect them to the d.c. power supply. Place the salt bridge and the copper half-cell in position before you start the electrolysis, as shown in Figure 1 on the next sheet.
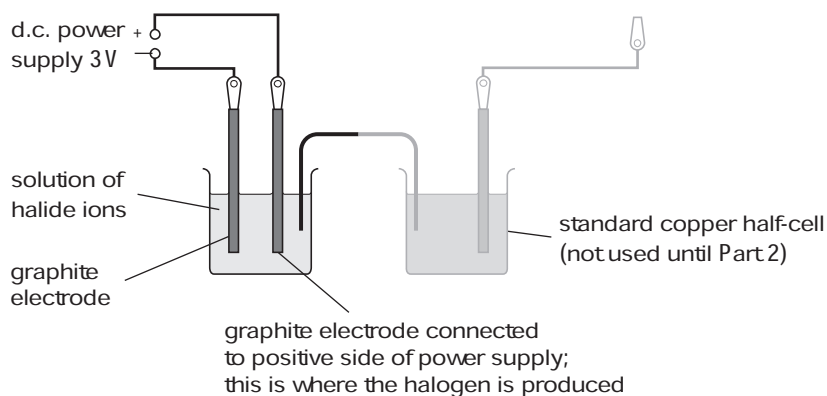
Figure 1 Arrangement for making the halogen/halide ion half-cell

3 Set the power supply to 3 V and pass a current through the potassium iodide solution for about 1 minute. The half-cell now contains both I^- ions and I_2.

4 It is essential that the halogen/halide ion half-cell is not disturbed in any way before you take the voltage reading in the next part of the activity. Disconnect the d.c. power supply. Take great care not to disturb the graphite electrode which was connected to the positive terminal. It is very important that the halogen deposited on the surface of the electrode is not lost.

Part 2: Making an electrochemical cell and measuring its voltage

5 Link the halogen/halide ion half-cell to the standard copper half-cell by connecting a high-resistance voltmeter into the circuit as shown in Figure 2. Record the voltage of the cell. Note whether the iodine/iodide half-cell is positive or negative with respect to the copper half-cell.
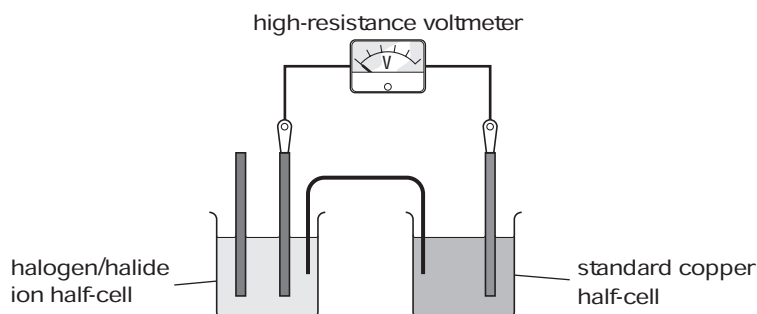

Figure 2 Arrangement for measuring the potential difference between a halogen/halide ion half-cell and a standard copper half-cell

Part 3: Using other halogen/halide ion half-cells

6 Repeat the procedure in Parts 1 and 2 using potassium bromide solution instead of potassium iodide solution. You must rinse the graphite electrode thoroughly to remove iodine, and then reconnect it to the positive terminal of the power supply.

7 Repeat the procedure once more, using potassium chloride solution.

QUESTIONS

Use **Chemical Ideas 9.2** to help you interpret the results of your experiment.

a A colourless gas is given off at the cathode (the negative electrode where reduction occurs) during the electrolysis in Part 1 of each experiment. What do you think the gas is?

b The electrode potential of the standard copper half-cell is +0.34 V. Use the values you obtained in the experiment to calculate electrode potentials for each of the halogen/halide ion half-cells.

c Compare these with the values of standard electrode potentials quoted on the **Data Sheets**.

Rusting is an electrochemical process. This activity will help you to work out the stages involved and why rusting takes place. You should then be able to understand some of the methods used to prevent corrosion.

Requirements

- test-tubes and rack
- watch-glasses (small and large)
- cottonwool
- petri dishes (3)
- iron filings (1 g)
- iron nails (3)
- emery paper
- ethanol
- copper metal foil (narrow strip)
- zinc metal foil (narrow strip)
- hydrochloric acid, $2.0 \, mol \, dm^{-3}$ ($2 \, cm^3$)
- sodium hydroxide solution, $2.0 \, mol \, dm^{-3}$ ($3 \, cm^3$)
- ferroxyl indicator solution ($200 \, cm^3$) (see advance preparation in the Teacher's and Technician's Guide)
- agar gel or gelatin (optional) (6 g)
- Bunsen burner
- dropping pipette
- piece of steel sheet ($16 \, cm^2$)

ethanol   HIGHLY FLAMMABLE

ferroxyl indicator   HARMFUL

sodium hydroxide solution   CORROSIVE

CARE Eye protection must be worn.   WEAR EYE PROTECTION

Introduction

Steel rusts because it reacts with the oxygen and the water in the atmosphere. In this activity, you will investigate the chemical changes that take place and find out how and why rusting happens.

Set out below are a number of experiments. None of them will give a complete answer, but by putting the information from all of them together, like pieces of a jigsaw, a complete picture will emerge.

Some of these experiments make use of *'ferroxyl' indicator.* This is a solution of sodium chloride containing Phenolphthalein and potassium hexacyanoferrate(III). It produces a blue colour with Fe^{2+} ions and a pink colour with OH^- ions.

What you do

In each experiment, observe carefully what happens and keep a careful record. In some cases you will need to leave the experiment set up for some time and make your observations at intervals.

Experiment 1

1 Add a few iron filings to a little $2.0 \, mol \, dm^{-3}$ hydrochloric acid in a test-tube. Warm to dissolve the filings. Iron(II) chloride and hydrogen gas are formed. (The smelly gas also given off is hydrogen sulphide, produced by reaction of the acid with impurities in the iron.)

2 Pour some of the solution onto a watch-glass. Add an excess of $2.0 \, mol \, dm^{-3}$ sodium hydroxide solution (**CARE** Corrosive), and leave the precipitate which forms exposed to the air for a little while.

    a Write a balanced ionic equation with state symbols for the reaction of iron filings with dilute acid.

    b Describe and explain what happened when sodium hydroxide solution was added to the solution on the watch-glass. Write an ionic equation with state symbols for the reaction you observed.

c Describe and explain what happened when the watch-glass was left exposed to the air. Write a half-equation to show what happened to the iron.

Experiment 2

3 In **Activity SS3.2** you made an electrochemical cell as shown in Figure 1. (There is no need to repeat the experiment here, but you need to remember what you did and what happened.)
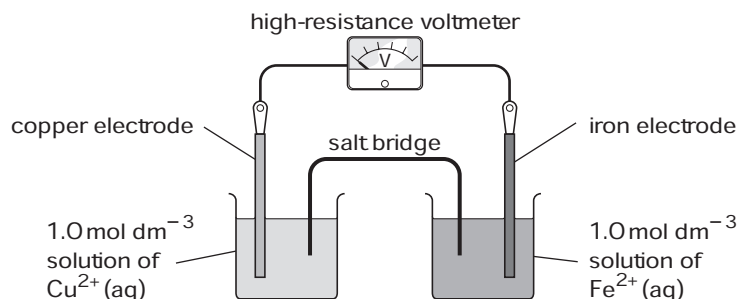
high-resistance voltmeter

copper electrode

salt bridge

iron electrode

$1.0 \, mol \, dm^{-3}$ solution of Cu^{2+} (aq)

$1.0 \, mol \, dm^{-3}$ solution of Fe^{2+} (aq)

Figure 1 An electrochemical cell made up of $Cu^{2+}(aq)/Cu(s)$ and $Fe^{2+}(aq)/Fe(s)$ half-cells

d Refer back to **Activity SS3.2**. What was the voltage of the cell (E_{cell})? Which half-cell was positive?

e If the voltmeter were removed from the circuit and replaced by an ammeter, a larger current would flow. Write a half-equation for the reaction taking place in each half-cell when this happens. In which half-cell is an oxidation taking place?

Experiment 3

4 Clean three iron nails by rubbing them carefully with emery paper, followed by a cloth moistened with ethanol.
Treat the nails as follows:
Nail A   No further treatment.
Nail B   Fold a narrow strip of copper foil in half, then push a nail between the two halves, slide the copper strip until it is just below the head of the nail, then crimp it tightly to make a good electrical contact, as in Figure 2.
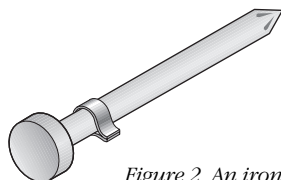
Figure 2 An iron nail in contact with copper

Nail C   Proceed as for nail B, but using zinc foil instead of copper.

5 Pour some 'ferroxyl' indicator into three petri dishes, to a depth of about 5 mm, and place the dishes over a sheet of white paper marked with the letters A, B and C in the positions where you expect to place the nails. Carefully place each nail in the 'ferroxyl' indicator solution above its appropriate letter and observe what happens over a period of about ten minutes. The 'ferroxyl' indicator solution should cover the nail completely.

   (Alternatively, you can use 'ferroxyl' indicator made up in an agar gel or gelatin. Add the nails and do not move the dishes until the gel is set. Cover and leave overnight. The gel will preserve the results.)

6 Record your observations in a table.

f For nail A, there are two main colour changes to the 'ferroxyl' indicator. Write half-equations for the reactions which have occurred at the surface of the nail to produce these colour changes.

g Compare the rate of corrosion of nail B with that of nail A. Explain your observations.

h Compare the rate of corrosion of nail C with that of nail A. What has formed on the surface of the zinc? Explain your observations.

Experiment 4

7 Onto a piece of clean steel put a drop of 'ferroxyl' indicator solution, about 2 cm in diameter. Cover the steel with a large watch-glass resting on a ring of cottonwool which is kept damp with water. Observe and record what happens within the drop. (You will need to leave this undisturbed for at least half an hour.)

   i Explain your observations.

Making sense of your results

Collect together the observations and results of all four experiments. Each one provides some relevant information about the rusting process. On the basis of these write a summary explaining how you think rusting takes place.

    You should now be able to explain why steel is covered with a thin layer of zinc (galvanising) to protect it from rusting. The steel does not rust even when the zinc coating is scratched.

—————————— **ADDITIONAL QUESTIONS** ——————————

   j Find out why 'ferroxyl' indicator solution turns blue in the presence of Fe^{2+} ions and pink in the presence of OH^- ions.

   k Suggest another metal which would behave in a way similar to zinc in protecting iron. Explain the reasons for your choice.

   l Why should copper rivets never be used to join together two pieces of iron?

   m Underwater steel pillars used to support piers are often found to corrode more severely when they are sunk beneath the sea bed than where they are in contact with sea water. Suggest a reason for this.

This activity will help you to make sure that you have understood the ideas met in **Activities SS3.1–SS3.4** *and in* **Chemical Ideas 9.2.**

As you investigate redox reactions in detail, a number of terms are introduced to help describe exactly what is happening, and to develop a way of recording and using data.

Go through the text of **Chemical Ideas 9.2** and make a list of the words and terms introduced. You can spot these easily because they are in **bold type**. Write a sentence or two explaining what each term means. If you find that difficult, work with someone else, and try explaining to your partner what you think each term means. Then write down what you agree is a clear explanation.

This activity illustrates two characteristic properties of transition metals: their abilities to form coloured compounds and to show a variety of oxidation states. You will use electrode potentials to help you interpret your results and to make predictions about redox reactions involving different oxidation states of vanadium. You can then compare your predictions with what you observe in practice.

Requirements

- $100 \, cm^3$ conical flask
- test-tubes (5) and rack
- $25 \, cm^3$ measuring cylinder
- ammonium vanadate(V) (ammonium metavanadate, NH_4VO_3) (0.25 g)
- sulphuric acid, $1.0 \, mol \, dm^{-3}$ ($25 \, cm^3$)
- concentrated sulphuric acid ($5 \, cm^3$)
- zinc powder (1–2 g) or a few pieces of granulated zinc
- cottonwool plug
- filter funnel and filter papers
- potassium manganate(VII) solution, $0.02 \, mol \, dm^{-3}$ ($10 \, cm^3$)
- iron(II) ammonium sulphate solution, $0.1 \, mol \, dm^{-3}$ ($2 \, cm^3$)
- potassium iodide solution, $0.05 \, mol \, dm^{-3}$ ($2 \, cm^3$)
- sodium thiosulphate solution, $0.1 \, mol \, dm^{-3}$ ($2 \, cm^3$)
- solid sodium sulphite, Na_2SO_3 (1 g)
- Bunsen burner
- access to fume cupboard
- protective gloves

ammonium vanadate(V) — TOXIC, IRRITANT

concentrated sulphuric acid — CORROSIVE

dilute sulphuric acid — IRRITANT

sulphur dioxide solution — HARMFUL

zinc powder — FLAMMABLE

**CARE** Eye protection and gloves must be worn. WEAR EYE PROTECTION, WEAR PROTECTIVE GLOVES

CARE Vanadium compounds are toxic. Avoid skin contact.

Background

Ammonium vanadate(V), NH_4VO_3, dissolves in moderately concentrated acid to give a yellow solution. Under these conditions, the ion present in solution can be thought of as the dioxovanadium(V) ion $VO_2^+(aq)$, but it actually polymerises to a more complicated species.

$$VO_3^-(aq) + 2H^+(aq) \rightarrow VO_2^+(aq) + H_2O(l)$$
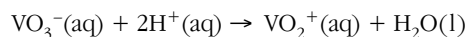
First, you will investigate the reduction of an acidic solution of vanadium(V) using zinc powder (or granulated zinc) as the reducing agent. Colour changes will indicate the formation of lower oxidation states of vanadium.

In the second part of the activity, you will investigate some changes between these oxidation states, using a variety of different oxidising and reducing agents.

You can use the standard electrode potentials in Table 1 to help you to explain your observations. You will also use this table to make predictions about some of the redox reactions. But remember, you can only predict whether a redox reaction is *energetically feasible* or not. Electrode potentials tell us nothing about the *rate* of the reaction. Sometimes reactions which are feasible can take place very slowly – so slowly that in practice they may not take place at all.

You can read about redox reactions and electrode potentials in **Chemical Ideas 9.2** and about the use of electrode potentials in predicting the direction of redox reactions in **Chemical Ideas 9.3.**

A2 LEVEL

Half-reaction	$E^{\ominus}$/V
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.44
$V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$	−0.26
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow SO_2(aq) + 2H_2O(l)$	+0.17
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$	+0.34
$I_2(aq) + 2e^- \rightarrow 2I^-(aq)$	+0.54
$S_2O_6^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow 2SO_2(aq) + 2H_2O(l)$	+0.57
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$VO_2^+(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$	+1.00
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51

Table 1 Standard electrode potentials at 298 K

Step-by-step reduction of vanadium(V)

1 First make up a solution of vanadium(V) as follows. Put about 0.25 g (one spatula load) of ammonium vanadate(V), NH_4VO_3 (**CARE** Toxic. Avoid skin contact), into a conical flask and add about 25 cm³ of 1.0 mol dm⁻³ sulphuric acid (**CARE** Irritant). Carefully add about 5 cm³ of concentrated sulphuric acid (**CARE** Extremely corrosive. Avoid skin contact) and swirl the flask until you obtain a clear yellow solution.

2 Pour about 2 cm³ of this vanadium(V) solution into each of *three* test tubes and keep for later investigations.

3 To the remaining solution in the conical flask, add a few pieces of granulated zinc (or a spatula load of zinc powder added a little at a time, with shaking). Plug the neck of the flask loosely with cottonwool to prevent the escape of acid spray. Gently swirl the flask until no further changes occur. (If you are using granulated zinc, heat the solution to speed up the reactions. Even with zinc powder, you may need to warm the flask gently to get the final colour change.)

a Describe what happens when the vanadium(V) solution reacts with zinc.

b Complete Table 2 to summarise the changes you have observed. (*Note* The first green colour you see is a mixture of the original vanadium(V) solution and vanadium(IV).)

Ion name	VO_2^+ dioxovanadium(V) ion	VO^{2+} oxovanadium(IV) ion	V^{3+} vanadium(III) ion	V^{2+} vanadium(II) ion
Oxidation state				
Colour				

Table 2 Oxidation states of vanadium and their colours

c Use the electrode potentials in Table 1 to explain your observations.

Oxidation of vanadium(II)

4 When the solution from step **3** has become violet, filter about 2 cm³ into a test-tube. Keep the remaining mixture in the flask.

5 Add to the test tube, a little at a time, an excess of acidified potassium manganate(VII) solution, shaking after each addition, until no further change is observed.

d Describe what happens. Are your results consistent with the electrode potentials in Table 1? Explain your answer.

Other redox reactions

Before you carry out each of the investigations in this section, first use the electrode potentials in Table 1 to *predict* what you think is likely to happen. Enter your predictions, and the colours you expect to see, in Table 3.

6 To one of the tubes containing $2\,cm^3$ of vanadium(V) solution, add about $2\,cm^3$ of iron(II) ammonium sulphate solution and mix thoroughly. (Iron(II) ammonium sulphate is a source of $Fe^{2+}(aq)$ ions.) The predictions and observations for this reaction have been entered in the table for you as a guide.

7 To the second tube containing $2\,cm^3$ of vanadium(V) solution, add about $2\,cm^3$ of potassium iodide solution and mix thoroughly. Then add about $2\,cm^3$ of sodium thiosulphate solution. (Thiosulphate ions reduce iodine to colourless iodide ions.)

8 To the third tube containing $2\,cm^3$ of vanadium(V) solution, add a little solid sodium sulphite, Na_2SO_3. (Sodium sulphite reacts with acid to produce a solution of sulphur dioxide, SO_2 (**CARE** Harmful).) Filter the mixture if cloudy and carefully boil the solution in a fume cupboard to remove the excess SO_2. Then add an equal volume of the violet vanadium(II) solution.

e Complete the results table (Table 3) for these three investigations. Interpret your observations carefully. For example, mixing blue and yellow solutions will give a green solution even if there is no chemical reaction at all.

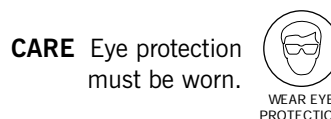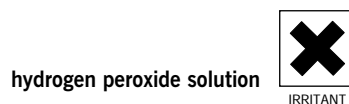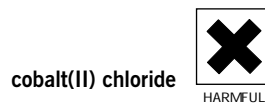|	Substances mixed	Predicted products	Predicted colour	Observation	Summary of reaction
6	$VO_2^+(aq) + Fe^{2+}(aq)$	$VO^{2+}(aq)$ and $Fe^{3+}(aq)$ blue yellow	green	green solution as predicted	$\overset{(+5)}{VO_2^+}(aq) \rightarrow \overset{(+4)}{VO^{2+}}(aq)$ $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$
7	$VO_2^+(aq) + I^-(aq)$ Then add thiosulphate				
8	$VO_2^+(aq) + SO_2(aq)$ Then add vanadium(II)				

Table 3 Results table

How do transition metal ions act as catalysts?

In this activity you will investigate the catalytic activity of aqueous cobalt(II) ions in the reaction between hydrogen peroxide and 2,3-dihydroxy-butanedioate ions. You will then use your observations to suggest a possible reaction pathway.
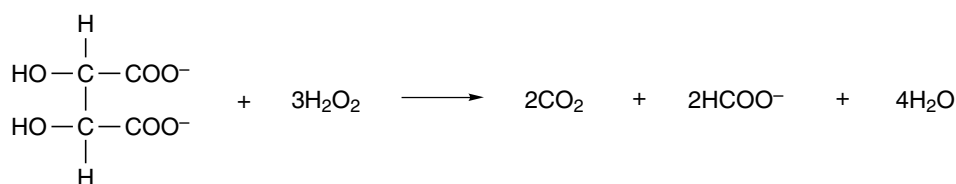
Requirements

- potassium sodium 2,3-dihydroxybutanedioate (potassium sodium tartrate or Rochelle salt) (2.5 g)
- 250 cm³ beaker
- 25 cm³ measuring cylinder
- Bunsen burner, tripod and gauze
- 0–110 °C thermometer
- hydrogen peroxide solution, 20 vol (20 cm³)
- 100 cm³ beaker
- cobalt(II) chloride, $CoCl_2.6H_2O$ (0.25 g)
- test-tubes (2) and rack
- ice bath

cobalt(II) chloride ✖ HARMFUL

hydrogen peroxide solution ✖ IRRITANT

CARE Eye protection must be worn. WEAR EYE PROTECTION

Background

Hydrogen peroxide can oxidise 2,3-dihydroxybutanedioate ions to carbon dioxide, methanoate ions and water:

$$HO-\overset{\overset{\displaystyle H}{|}}{C}-COO^- \quad HO-\overset{}{\underset{\underset{\displaystyle H}{|}}{C}}-COO^- \quad + \quad 3H_2O_2 \quad \longrightarrow \quad 2CO_2 \quad + \quad 2HCOO^- \quad + \quad 4H_2O$$

The reaction is energetically feasible, but takes place very slowly, even when heated. The problem is the high activation enthalpy which provides a kinetic barrier to reaction.

The reaction can be speeded up by adding cobalt(II) ions.

What you do

1 Dissolve about 2.5 g of potassium sodium 2,3-dihydroxybutanedioate in 50 cm³ of water in a 250 cm³ beaker. Heat the solution to about 70 °C.

2 Heat 20 cm³ of hydrogen peroxide solution (**CARE** Irritant) to approximately the same temperature in a 100 cm³ beaker, and add to the warm solution of 2,3-dihydroxybutanedioate ions from step **1**.

3 Remove the beaker from the heat and stand it on a mat. Monitor the temperature of the solution for a few minutes and note any changes in appearance.

4 Dissolve about 0.25 g of cobalt(II) chloride (**CARE** Harmful. Avoid skin contact) in about 5 cm³ of distilled water in a test-tube and add this to the hot solution. Keep the thermometer in the reaction mixture to monitor the temperature, but do not stir. **Stand back until a reaction takes place** – there will be a short delay before anything happens. Note any changes.

5 Repeat the reaction in steps **1–4**, but when the solution becomes dark green quickly transfer about 5 cm³ to a test-tube which has been immersed in an ice bath. Replace the tube in the ice bath. After a while allow the mixture to warm to room temperature.

6 Write a brief summary of the reactions you have carried out and what you have observed.

_____**QUESTIONS**_____

a Describe what happened when you mixed the hydrogen peroxide solution and the solution of 2,3-dihydroxybutanedioate ions.

b What colour is the aqueous cobalt(II) ion, $[Co(H_2O)_6]^{2+}(aq)$?

c Cobalt(III) ions are not stable in aqueous solution. (They are reduced by water to cobalt(II) ions.) They can be stabilised in aqueous solution by adding certain ions or molecules, such as carboxylate ions, which complex with the cobalt.

Suggest a substance which might be responsible for the dark green colour observed during the reaction.

d Suggest how the substance responsible for the green colour might have been formed. (There is no need to give any equations.)

e Suggest why the dark green solution eventually returns to its original pink colour.

f Why does cooling the test-tube preserve the green colour for a while?

g Suggest a possible mechanism for the catalysed hydrogen peroxide oxidation of 2,3-dihydroxybutanedioate ions by cobalt(II) ions. (There is no need to give any equations.)

h Are the cobalt ions behaving as a homogeneous or a hetereogeneous catalyst? Explain your answer.

i What two properties of cobalt ions are important to their ability to catalyse this reaction?

j Draw enthalpy profile diagrams (on the same axes) for the catalysed and uncatalysed reactions.

k In two sentences, summarise the role of a catalyst in a reaction.

> *Transition metals form a wide variety of complexes, many of which are highly coloured. In the first part of this activity, you will make some complexes of nickel and investigate their relative stability. You will then look at complexes of other transition metal ions and compare the reactions of copper(II), iron(II) and iron(III) ions with sodium hydroxide and ammonia.*

Requirements

- rack with 5 test-tubes and boiling tube
- nickel(II) chloride, $NiCl_2.6H_2O$ (1 g)
- concentrated hydrochloric acid (2 cm^3)
- sodium hydroxide solution, 2.0 mol dm^{-3} (20 cm^3)
- concentrated ammonia solution (5 cm^3)
- disodium salt of H_4edta (Na_2H_2edta), 0.1 mol dm^{-3} (5 cm^3)
- copper(II) sulphate solution, 1 mol dm^{-3} (4 cm^3)
- ammonia solution, 2 mol dm^{-3} (20 cm^3)
- iron(II) sulphate solution, 1 mol dm^{-3} (4 cm^3)
- iron(III) chloride solution, 1 mol dm^{-3} (4 cm^3)
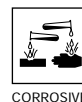- access to fume cupboard

concentrated ammonia solution — CORROSIVE

dilute ammonia solution — IRRITANT

copper(II) sulphate solution — HARMFUL

concentrated hydrochloric acid — CORROSIVE

iron(III) chloride solution — IRRITANT

nickel(II) chloride — HARMFUL

sodium hydroxide solution — CORROSIVE
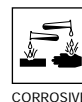
CARE Eye protection must be worn. — WEAR EYE PROTECTION

Introduction

When you add a substance which can act as a ligand to a solution containing complex ions, the new ligands will compete with the existing ligands for the metal ion and a new complex may be formed. Reactions like these, in which one ligand is replaced by another, are called **ligand exchange reactions.**

Ligand exchange reactions are easy to observe because a change of ligand usually results in a change of colour. If one ligand complexes with the metal ion much more strongly than the other, the position of equilibrium will be in favour of the more stable complex, and the reaction will appear to go to completion in that direction.

The stability of a complex can be expressed in terms of the equilibrium constant for the overall ligand displacement reaction. This is known as the **stability constant,** K_{stab}. The higher the value of the stability constant, the more stable the complex.

Stability constants can be used to compare the stability of any two complexes, but the values usually quoted give the stability of a complex relative to the simple aqueous ions, where water is the ligand.

You can read about ligand displacement reactions and stability constants in **Chemical Ideas 11.6.**

Part 1: Some complexes of nickel(II) ions

Carry out the following reactions in order *in the same boiling tube*. After each step, transfer a small quantity of the mixture to one of the test-tubes to keep for comparison.

1 To a few crystals of solid nickel(II) chloride (**CARE** Harmful) in a boiling tube, add about $2\,cm^3$ of concentrated hydrochloric acid (**CARE** Corrosive) and shake gently until the crystals dissolve.

   a A complex ion is formed with the formula $[NiCl_4]^{2-}(aq)$. What is the colour of this complex and what ligand does it contain? What is the coordination number of the complex?

2 Now add an equal volume of water to the boiling tube.

   b What is the colour of the solution now? What ligand is present in the new complex ion? This ion has a coordination number of 6. Write the formula of the ion.
   c Write an equation with state symbols for the reaction you observed in step **2**.

3 Add sodium hydroxide solution (**CARE** Corrosive) drop by drop to the solution in the boiling tube until a precipitate just forms.

   d Give the name and formula of the precipitate and write an equation with state symbols for the reaction you have observed.

4 Now, using a fume cupboard, carefully add concentrated ammonia solution (**CARE** Irritant. Gives off irritating vapours) to the precipitate in the boiling tube. Continue adding until you have a solution again.

   e What is the colour of the solution? What ligand is now present? The new complex ion formed has a coordination number of 6. Write the formula of the ion and an equation with state symbols for the reaction.

5 Finally, add a solution of the disodium salt of H_4edta (Na_2H_2edta) to the mixture in the boiling tube.

   f H_4edta contains four carboxylic acid groups, –COOH, as well as two amino groups. In alkaline solution, it forms the $edta^{4-}$ ion. (Edta is an abbreviation of its old name.)
      $Edta^{4-}$ is an unusual ligand because it can form six bonds with the central metal ion. It wraps itself around the nickel ion enclosing it in a cage-like structure. The complex with nickel has the formula $[Ni\,edta]^{2-}$. What is the colour of this complex? Write an equation with state symbols for the reaction you have observed.

6 Summarise your results by filling in a copy of Table 1.

Procedure	Observations	Formula of nickel complex (or nickel compound) formed
1 Addition of concentrated hydrochloric acid to solid nickel(II) chloride		
2 Addition of an equal volume of water		
3 Addition of sodium hydroxide solution drop by drop until precipitate just forms		
4 Addition of concentrated ammonia solution		
5 Addition of $edta^{4-}$ ions		

Table 1 Results table

   g Are your results in reactions **4** and **5** consistent with the following overall stability constants for nickel complexes?

| ligand	lg K_{stab}
NH_3	8.6
$edta^{4-}$	19.3

   h For the complex $[Ni(CN)_4]^{2-}$, lg $K_{stab} = 31$. What would be the effect of adding $edta^{4-}$ ions to a solution of $[Ni(CN)_4]^{2-}$ ions in water?

A2 LEVEL

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

7 Add about $2\,cm^3$ of copper(II) sulphate solution (**CARE** Harmful) to a boiling tube.

    i The characteristic blue colour is that of a complex ion with coordination number 6. What is the ligand and what is the formula of the ion?

8 Add about $1\,cm^3$ of sodium hydroxide solution to the solution in the tube, shake the tube and note the colour of the precipitate formed.

    j Give the name and formula of the precipitate and write an ionic equation, with appropriate state symbols, for the reaction you have observed.

9 Now, using a fume cupboard, carefully add concentrated ammonia solution to the precipitate in the boiling tube. Continue adding, with shaking, until you have a solution again.

    k What is the colour of the solution? Four of the water ligands have been replaced by ammonia ligands. What is the formula of the new complex ion?

A dilute solution of ammonia is a weak base and so can act as a source of $OH^-(aq)$ ions as well as NH_3 ligands:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
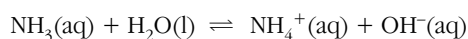
    l Predict what you would observe if you slowly add a dilute solution of ammonia to a solution of copper(II) sulphate until the ammonia is in excess.

10 Test your prediction by slowly adding dilute ammonia solution to about $2\,cm^3$ of copper(II) sulphate solution in a boiling tube.

11 Construct a table similar to Table 2 and use it to summarise your results for copper(II) ions.

12 Then carry out the necessary tests to enable you to complete your table for iron(II) ions and iron(III) ions. Use iron(II) sulphate solution as a source of iron(II) ions and iron(III) chloride (**CARE** Irritant) as a source of iron(III) ions.

Transition metal ion	Observations:	
	when dilute sodium hydroxide solution is added	when dilute ammonia solution is added slowly
copper(II)		
iron(II)		
iron(III)		

Table 2 Results table

    m Write ionic equations, with state symbols, which could explain your observations for the iron(II) and iron(III) tests.

Use this list as the basis of a summary of the unit by collecting together the related points and arranging them in groups. Check that your notes cover the points and are organised in appropriate ways. Remember that you will be coming back to some of the ideas in later units.

Most of the points are covered in the **Chemical Ideas**, with supporting information in the **Storyline** or **Activities**. However, if the *main* source of information is the Storyline or an Activity, this is indicated.

- The range of types, properties and uses of steel (**Storyline SS1** and **SS2**).

- The importance of the composition of a steel in determining its properties (**Activity SS2.5**).

- Redox processes that occur during steelmaking (including removal of sulphur and the reactions during the oxygen blow) (**Storyline SS2**; **Activities SS2.2–2.4**).

- How some substances appear coloured because they absorb radiation in specific parts of the visible spectrum.

- The use of colorimetric measurements to determine the concentration of a coloured solution (**Activity SS1.1**).

- The procedure for carrying out a simple redox titration involving manganate(VII) ions and how to work out the results (**Activity SS1.2**).

- Transition metals are d-block elements that form one or more stable ions with incompletely filled d orbitals.

- Typical properties of transition metals in the first row of the d block with particular reference to iron and copper: existence of more than one oxidation state for each element in its compounds, formation of coloured ions in solution, reactions with ligands to form complexes and reactions involving ligand substitution, catalytic behaviour of the elements and their compounds.

- The reactions of $Fe^{2+}(aq)$, $Fe^{3+}(aq)$ and $Cu^{2+}(aq)$ ions with sodium hydroxide solution and ammonia solution (**Activity SS5.3**).

- The variable oxidation states of transition metals in terms of electronic energy levels.

- The catalytic activity of transition metals and their compounds in terms of variable oxidation states (**Activity SS5.2**).

- The meaning of the terms: *ligand*, *complex/complex ion* and *ligand exchange*.

- The formation of complexes in terms of bonding between ligands and central metal ion.

- The meaning of the term *polydentate* as applied to ligands, exemplified by $edta^{4-}$.

- The shapes of complexes with coordination numbers 4 and 6.

- Ligand exchange reactions and stability constants.

- Redox reactions of d-block elements in terms of electron transfer, and represented by (i) using half-equations for the oxidation and reduction reactions and (ii) combining half-equations to give the overall equation for the reaction.

- The construction of simple electrochemical cells involving metal ion/metal half-cells, and half-cells based on different oxidation states of the same element in aqueous solution.

- The meaning and use of the term: *standard electrode potential*; how a standard electrode potential is measured.

- The action of an electrochemical cell in terms of half-equations and external electron flow.

- The use of standard electrode potentials to calculate E_{cell}, and to predict the feasibility of redox reactions and the relative stability of oxidation states.

- Rusting in terms of electrochemical processes involving iron and oxygen (**Storyline SS3**; **Activity SS3.4**).

- The effect of complex formation on the rate of corrosion.

- Approaches to the recycling of iron (**Storyline SS4**).

A2 LEVEL