Salters Advanced Chemistry
Module 3 Activities Booklet

Chemistry of Materials

2849

DP	Designer Polymers
EP	Engineering Proteins
SS	The Steel Story

Unit WM *(What's in a Medicine?)* is examined as part of this module (2849), but we've put the activities from WM in the 2848 Activities Booklet (the pink one).

Chemistry of Materials

Module 3 – 2849 - Activities Booklet

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DP2.1

Making nylon

***A nylon is made from its monomers by condensation polymerisation. You may already have done this or a similar experiment in an earlier course. If so, you can omit this activity and go on to* Activity DP2.2.**

Requirements

- 5 cm^3 beaker
- decanedioyl dichloride, 5% solution in cyclohexane (1 cm^3)
- 1,6-diaminohexane, 5% solution in 0.5 mol dm^{-3} sodium carbonate solution (1 cm^3)
- glass rod or test-tube
- tweezers
- access to fume cupboard
- protective gloves

cyclohexane

decanedioyl dichloride

1,6-diaminohexane

CARE Eye protection and gloves must be worn.

What you do

1 Pour about 1 cm^3 of the 1,6-diaminohexane solution (**CARE** Irritant) into a 5 cm^3 beaker.

2 Carefully add an equal volume of the decanedioyl dichloride solution to the beaker. (**CARE** Decanedioyl dichloride has an irritating vapour. The vapour is a powerful **lachrymator** (eye irritant) and this effect is often delayed. *Perform this part of the activity in a fume cupboard*.)

Two separate layers will form. Do not mix them.

3 Use a pair of tweezers to remove the nylon film which forms where the two layers are in contact. Do this slowly and hook the nylon thread which forms onto a glass rod or a test-tube.

Slowly wind the thread around the rod. As the nylon is removed more forms at the solution interface, so you should be able to keep on winding for some time.

4 Once you have made some nylon it needs to be washed thoroughly with tap water. *Take care not to touch the nylon* because it forms as a hollow tube, and there will still be some chemicals trapped in the middle.

QUESTIONS

a Write out an equation to show the formation of nylon in this activity.

b What is the name of the nylon you have made?

DP2.2

Taking nylon apart

In this experiment you are going to convert some nylon-6,6 polymer back into its original di-acid and di-amine. The linkages in the nylon are broken down by hydrolysis using sulphuric acid. This activity will allow you to improve your skill in carrying out an organic reaction safely. You will learn how to purify an organic solid and how to measure its melting point.

Requirements

- nylon-6,6 granules (2 g)
- 100 cm^3 boiling flask
- condenser
- sulphuric acid, 30% (35 cm^3)
- 250 cm^3 conical flasks (2)
- watch-glass
- thin-walled capillary tubes (or melting-point tubes)
- melting-point apparatus for use up to 150 °C
- apparatus for vacuum filtration
- saturated sodium hydrogencarbonate solution (20 cm^3)
- sodium hydroxide solution, 2 mol dm^{-3} (5 cm^3)
- 100 cm^3 measuring cylinder
- ice
- electric heating mantle
- 250 cm^3 beakers (2)
- 10 cm^3 measuring cylinder
- Universal Indicator paper

sodium hydroxide solution

sulphuric acid

CARE Eye protection must be worn throughout.

CARE Sulphuric acid of this concentration is very corrosive.

Introduction

If you did **Activity DP2.1** you will have made a nylon from its monomers by condensation polymerisation. A reaction like this, in which a new substance is made from simpler substances, is called a **synthesis**.

The reverse process, in which a large molecule is broken down into simpler molecules, is called a **degradation.** This type of reaction is often used by chemists to find out about the composition of substances. If they can identify the degradation products, they may be able to work out the structure of the original compound.

The amide linkages in nylon can be **hydrolysed** (split by water) to give the parent di-acid and di-amine. The reaction with water is very slow indeed, but it can be speeded up by carrying out the hydrolysis in acid solution (**acid hydrolysis**). You will use moderately concentrated sulphuric acid (about 5.5 mol dm^{-3}) for the hydrolysis.

What you do

Part 1: Breaking down the nylon

1 Place 2 g of nylon-6,6 granules into a 100 cm^3 flask to which a reflux condenser can be attached.

2 Pour 35 cm^3 of 30% sulphuric acid into the flask. (**CARE** Sulphuric acid of this concentration is very corrosive.) Fit the condenser to the flask (Figure 1).

3 Place the reaction flask and condenser in the heating mantle. Heat the reaction mixture under reflux for about 3 hours. (This technique is used when you want to heat reactants for some time, but not lose either the reactants or the products by evaporation.) Add a few boiling chips to help the mixture boil smoothly.

The nylon will all have dissolved after about 45 minutes, but you should carry on heating to complete the degradation.

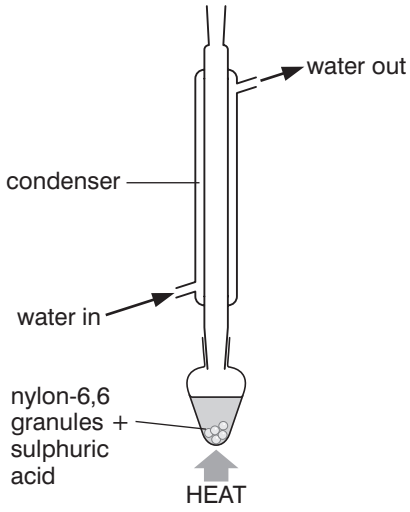


Figure 1 Breaking down the nylon

4 Allow the flask and contents to cool, then place them in an ice bath and leave them overnight for crystals to form.
5 Collect the crystals by vacuum filtration. Keep the filtrate for use later.

Part 2: Purifying the hexanedioic acid by recrystallisation

Your solid now needs to be purified by **recrystallisation**.

6 Place your hexanedioic acid crystals in a 250 cm^3 conical flask. Add 10 cm^3 of distilled water. Hold the neck of the flask with an insulating holder and gently heat the flask, swirling the contents at the same time. If some crystals remain when the water starts to boil, add a further 5 cm^3 of water and reheat.
7 Carry on in this way until all the crystals have dissolved in the minimum quantity of water.
8 If your solution is clear, you can loosely cover the opening to the flask and leave the solution to cool overnight.

If the solution contains debris, this can be removed by carefully decanting most of the solution into a second flask, leaving the debris behind. You will need to reheat the solution to redissolve the crystals before covering it and leaving it to recrystallise.

9 Collect the crystals by vacuum filtration and leave them to dry on a watch-glass. To speed things up you can place the watch-glass in an oven or on a food-warming tray.

Part 3: Finding a melting point

Hexanedioic acid melts at 152 °C. Find the melting point of your crystals and compare it with this value.

This is what you do to determine a melting point.

10 Carefully heat one end of a small thin-walled capillary tube – a melting-point tube – so that the opening is just sealed. Leave the tube to cool.
11 Grind a small quantity of your dry crystals in one corner of the watch-glass until you have a fine powder.

Tap the open end of the melting-point tube into the fine powder so that a little powder packs into the tube. Invert the tube and tap it gently so that the powder falls to the closed end. Your teacher may show you an effective way of doing this. Do not try to put too much powder into the tube at once.

12 Repeat the procedure until you have about 1 cm depth of powder in the tube.
13 You may have an electrically-heated melting point apparatus which your teacher will show you how to use. Another way of determining melting points is described next.
14 Fix the tube into position in the melting-point apparatus as shown in Figure 2.

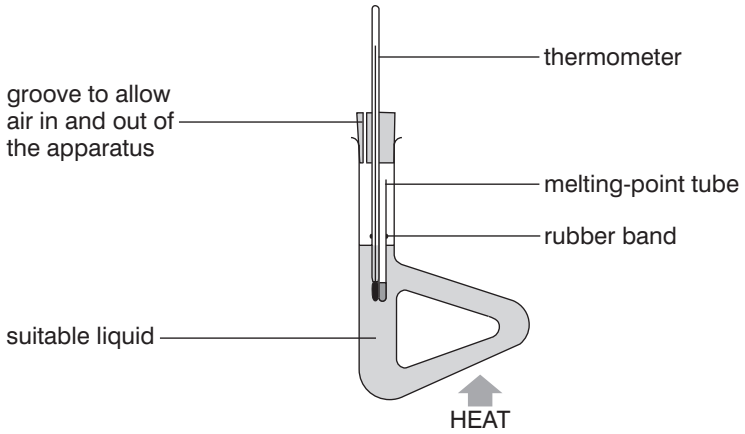


Figure 2 Melting-point apparatus

15 Slowly heat the side-arm of the apparatus with a very low Bunsen burner flame. The design of the apparatus should ensure a circulation of warm liquid around the sample and thermometer. Watch the sample carefully. When it melts, the powder will collapse into a sticky liquid. Record the temperature at which this happens.

16 This will be a rough value for the melting point because you were heating quite quickly. To determine an accurate melting point, allow the apparatus to cool down to about 10 °C below the value you have just recorded. Prepare another sample while this is happening. Then repeat the process with the fresh sample and a slower rate of heating.

17 Record the accurately determined melting point of your hexanedioic acid.

Part 4: Detecting the 1,6-diaminohexane produced

The diamine is still in solution in the filtrate obtained in Part 1 because it has formed a soluble salt by reacting with the sulphuric acid.

18 Take 5 cm^3 of the filtrate and carefully pour it into 20 cm^3 of saturated sodium hydrogencarbonate solution in a 250 cm^3 beaker. (**CARE** Do not add the filtrate all in one go or the mixture will fizz dangerously.)

Use pH paper to make sure that the mixture is no longer acidic. If necessary add some more sodium hydrogencarbonate solution to achieve this.

19 Then add 5 cm^3 of 2 mol dm^{-3} sodium hydroxide solution to make the solution alkaline. (**CARE** Sodium hydroxide solution is corrosive.) Cautiously swirl the contents of the beaker and note the smell of the solution which contains 1,6-diaminohexane. (For comparison, the trivial names of 1,4-diaminobutane and 1,5-diaminopentane are putrescine and cadavarine respectively, both of which are associated with the putrefaction of proteins in flesh.)

QUESTIONS

a What property of hexanedioic acid is made use of in the recrystallisation process?

b Melting points are often used to identify compounds. They are also a good indication of the purity of a compound. Was your sample of hexanedioic acid pure? Explain your answer.

c Write an equation for the hydrolysis of a short section of nylon-6,6 to produce hexanedioic acid and 1,6-diaminohexane.

DP4

Comparing models of nylon-6,6 and Kevlar

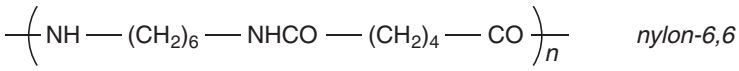
One thing you will achieve from studying this unit is an understanding of how the properties of polymers relate to their structures. In this activity you can examine this relationship for nylon and Kevlar.

Requirements

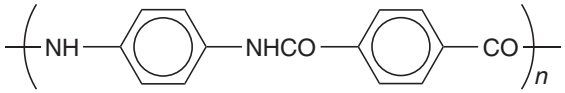
- molecular model kit

Building the model

The structures of the polymers nylon-6,6 and Kevlar are:



nylon-6,6



Kevlar

Use your model kit to make the structures that represent the repeating units for these polymers. Then join your nylon model together with those from other students' kits to make a long-chain model of the polymer. Do the same for the Kevlar structure. Use your models to help you work through the questions which follow.

QUESTIONS

a How do the models of the polymer chains behave when stretched? Which polymer will be more elastic?

b Use the models to explain the following data, which were obtained in experiments to test the strengths of the two polymers:

	Elongation at fracture
nylon-6,6	18%
Kevlar	3%

c The bond lengths in Kevlar and nylon-6,6 can be estimated from comparable functional groups in other organic molecules:

		Bond length/nm	
		nylon-6,6	Kevlar
N–C	(in CONH group)	0.132	0.132
N–C	(attached to a hydrocarbon group)	0.147	0.135
C–C	(in a hydrocarbon group)	0.154	0.139
C–C	(attached to CONH group)	0.150	0.148

There is usually a good correlation in chemistry between bond length and bond strength: shorter bonds are stronger, longer bonds are weaker.

i Draw the structures of nylon-6,6 and Kevlar, and mark on each of them the bond lengths from the table.

ii Use the bond lengths to explain why Kevlar is more stable than nylon-6,6 when heated.

DP5

Bubble gum – or bubble glass?

The polymer in bubble gum can be elastic or glassy, depending on temperature. You can study both forms with the help of a domestic freezer.

Requirements

- bubble gum (eg Hubba Bubba)
- freezer

CARE Do this experiment at home, not at school.

CARE Do not handle other people's bubble gum.

What you do

1 Chew a piece of bubble gum until all the taste has gone.

2 Gently pull the gum and then release it.

a Does it show any elastic properties?

3 Pull it so that it stretches to about eight times its original length.

b Does it still show elastic properties? Does it completely return to its original length? What term is used to describe this irreversible change?

4 Now shape your piece of bubble gum so it's about the same size as a 5p coin. Wrap it in some plastic film and place it in the coldest part of your freezer for about 15 minutes.

When you remove the gum from the freezer, quickly bend it.

c What happens? Can you explain the result? What happens as it returns to room temperature?

DP8

Check your notes on *Designer Polymers*

This activity helps you get your notes in order at the end of this unit.

Use this list as the basis of a summary of the unit by collecting together the related points and arranging them in groups. You may also wish to check how this unit has further developed ideas first met in **The Polymer Revolution**. You may want to link the summaries of parts of **The Polymer Revolution** to the summaries you prepare for this unit.

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 historical development of condensation polymers (polyamides and polyesters) (**Storyline DP2** and **DP3**).
- How to distinguish between addition and condensation polymerisation.
- Predicting the structural formula of the condensation polymer formed from given monomer(s) and vice versa.
- The hydrolysis of esters.
- Be able to recognise members of the following homologous series: amines and amides.
- The use of systematic nomenclature to name primary amines.
- The characteristic properties of the amino group, including: basic nature and acylation.
- The reaction between a primary amine and an acyl chloride to produce an amide.
- The hydrolysis of an amide (**Activity DP2.2**).
- The procedure for purifying an organic solid product (**Activity DP2.2**).
- The properties of condensation polymers in terms of intermolecular attractions.
- The effect of temperature changes on polymers.
- The relationship between the properties of polymers and their molecular structure.
- The ways that chemists can modify the properties of a polymer by physical and chemical means (including the use of co-polymers), to meet particular needs.
- The use of given data to design a polymer for a particular purpose.
- The disposal and recycling of polymers (**Storyline DP7**).

EP2.I

Investigating amines and amino acids

In this activity you will compare the properties of amines and amino acids, using butylamine as an example of an amine and glycine as an example of an amino acid.

Requirements

- Universal Indicator paper
- test-tubes (8) and rack
- butylamine (2 cm^3)
- glycine (aminoethanoic acid) (2 g)
- concentrated hydrochloric acid (a few drops)
- sodium hydroxide solution, 2 mol dm^{-3} (10 cm^3)
- hydrochloric acid, 0.01 mol dm^{-3} (1 cm^3)
- sodium hydroxide solution, 0.01 mol dm^{-3} (2 cm^3)
- copper(II) sulphate solution, 0.1 mol dm^{-3} (2 cm^3)
- ethanoyl chloride (2 cm^3)

butylamine


IRRITANT


HIGHLY FLAMMABLE

ethanoyl chloride


CORROSIVE


HIGHLY FLAMMABLE

hydrochloric acid


CORROSIVE

sodium hydroxide solution


CORROSIVE

CARE Butylamine and ethanoyl chloride are volatile and have unpleasant, highly flammable vapours. Use the bottles in a fume cupboard and avoid inhaling the vapours.

CARE Eye protection must be worn.


WEAR EYE PROTECTION

What you do

Carry out the tests in Part 1 on butylamine, an example of an amine. Then carry out a similar series of tests in Part 2 on glycine, an example of an amino acid. Before you start, read through the tests and draw up a suitable table in which to record your observations. Your table should allow you to compare the behaviour of the two compounds.

Part 1: Reactions of an amine

1 Solubility Add a few drops of butylamine (**CARE** Highly flammable; irritant vapour) to 1 cm depth of water in a test-tube.

a Is butylamine soluble in water? Explain any solubility in terms of interactions between the particles concerned.

b Record the pH of any solution which has been formed. Write an equation to explain any change to the pH of the water.

2 Adding acid and alkali Add a few drops of concentrated hydrochloric acid (**CARE** Corrosive) to the butylamine solution from test **1**. Make a note of any changes, including smell, before and after addition of the acid (**CARE** Take very great care when smelling the vapours. Just gently waft your hand over the mouth of the test-tube towards your nose. Keep your head well away from the tube. Do this experiment *very* cautiously.). Then add about 2 cm depth of 2 mol dm^{-3} sodium hydroxide solution (**CARE** Corrosive) and shake the tube gently; again, note any changes.

c Write equation(s) for any changes you have noted.

3 Reaction with copper(II) sulphate Add a few drops of butylamine to 1 cm depth of copper(II) sulphate solution in a test-tube. Make a note of any changes which occur.

d Write down the formula of any new copper-containing particles which may have been formed.

4 Adding ethanoyl chloride Place 10 drops of butylamine in a dry test-tube. Add 10 drops, *one drop at a time*, of ethanoyl chloride (**CARE** Highly flammable and corrosive. **Can react violently**).

e Make a note of the results, and write an equation for any reaction which occurs.

Add 1 cm depth of water to the tube and carefully stir the mixture. Then add 3 cm depth of 2 mol dm^{-3} sodium hydroxide solution. Warm the mixture, and hold a piece of moistened pH paper at the mouth of the test-tube.

f Explain any change to the pH paper in terms of the process occurring in the test-tube.

Part 2: Reactions of an amino acid

5 Solubility Add a few crystals of glycine to 1 cm depth of water in a test-tube.

g Is glycine soluble in water? Explain any solubility in terms of interactions between the particles concerned.

h Record the pH of any solution which has been formed.

6 Adding acid and alkali Add 1 cm depth of 0.01 mol dm^{-3} hydrochloric acid, in two separate 0.5 cm depth portions, to the glycine solution from test **5**. Then add 2 cm depth of 0.01 mol dm^{-3} sodium hydroxide in four separate 0.5 cm depth portions. Record the pH after each addition.

i Use your knowledge of the acid-base properties of an amino acid like glycine to explain how the pH of the solution behaves during the addition of acid or alkali.

7 Reaction with copper(II) sulphate Add a few crystals of glycine to 1 cm depth of copper(II) sulphate solution in a test-tube. Make a note of any changes which occur.

j Compare the behaviour of butylamine and glycine with copper(II) sulphate solution.

8 Adding ethanoyl chloride Place a few crystals of glycine into a dry test-tube, and repeat the procedure in test **4**.

k Compare the behaviour of butylamine and glycine with ethanoyl chloride.

Comparison

l Make a note of the similarities between the reactions of butylamine (an amine) and glycine (an amino acid).

m Explain any differences in the chemical properties of the two types of compound.

n Suggest why butylamine is a low-boiling liquid but glycine is a high-melting crystalline solid.

EP2.2

What's in aspartame?

Is this activity you will apply your skills at chromatography to help you investigate the conditions needed for the hydrolysis of peptide bonds. You will be looking at a simple example: aspartame, a dipeptide used as an artificial sweetener. You will be investigating what concentration of acid, and what reflux time, are needed to hydrolyse the dipeptide.

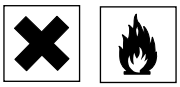
Requirements

- aspartame, eg Searle 'Canderel' tablets (1–3 tablets)
- hydrochloric acid: various concentrations, eg 4 mol dm^{-3}, 2 mol dm^{-3}, 1 mol dm^{-3} (25 cm^3 each)
- 10 cm^3 measuring cylinder
- apparatus for heating under reflux, eg 50 cm^3 pear-shaped flask and water condenser
- anti-bumping granules
- apparatus for paper chromatography
- 250 cm^3 beaker
- butan-1-ol (20 cm^3)
- glacial ethanoic acid (4 cm^3)
- separating funnel
- aspartic acid solution, 0.01 mol dm^{-3}
- phenylalanine solution, 0.01 mol dm^{-3}

} small amounts for chromatography

- ninhydrin in butan-1-ol, 0.5% solution in spray bottle
- mortar and pestle
- hair dryer
- protective gloves

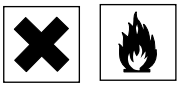
butan-1-ol



ethanoic acid

hydrochloric acid

ninhydrin solution



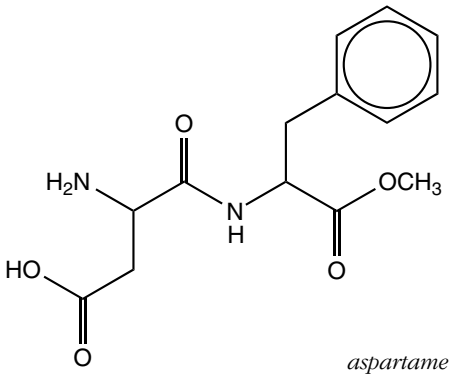
CARE Eye protection must be worn.

CARE Ninhydrin solution must be used in a fume cupboard. Gloves must be worn. Wash the solution off with lots of soap and water if it contacts your skin.

Introduction

Peptide bonds in proteins can be hydrolysed by refluxing with hydrochloric acid. You will use the artificial sweetener aspartame as a substitute for a protein in this activity. Aspartame is the methyl ester of the dipeptide Asp Phe. The ester link in aspartame will also be hydrolysed under these conditions, so you will get aspartic acid and phenylalanine just as you would from the dipeptide itself.

The skeletal formula for aspartame is shown below.



aspartame

What you do

You are to investigate what concentration of acid and what reflux time are sufficient to hydrolyse the aspartame in one tablet.

You can use your skill at chromatography to analyse your reaction products to find out whether the free amino acids are present in reasonable quantities. (Some tablets contain phenylalanine with the aspartame so you must detect *both* phenylalanine *and* aspartic acid to be sure hydrolysis has occurred.)

The chromatography solvent can be made by shaking together butan-1-ol (**CARE** Harmful and flammable), glacial ethanoic acid (**CARE** Corrosive; avoid inhaling the vapour) and water in the ratio 5:1:4 by volume in a separating funnel. When the mixture settles, two layers will form. Use the upper, non-aqueous layer as your solvent.

Amino acids can be detected by spraying the paper with ninhydrin solution (**CARE** Harmful, flammable; observe the safety warnings above) and then warming the paper, for example using a hair dryer. **Do not use a flame**. The spots may be slow to develop. Circle them with pencil when they appear, as they will fade.

QUESTION

Write an equation for the hydrolysis of aspartame, showing the skeletal formulae of the three products formed.

EP2.3

Using nuclear magnetic resonance (n.m.r.) spectroscopy for structure determination

In this activity you will have practice in analysing n.m.r. spectra of organic compounds.

Introduction

In Part 1 of this activity you will analyse the n.m.r spectra of a range of simple organic compounds. In Part 2, the n.m.r spectra of three different nitrogen-containing compounds, one of which is the analgesic paracetamol, will be considered. You will then be asked to make predictions about the infrared spectrum of paracetamol.

The typical resonance positions for various hydrogen atoms, expressed as chemical shifts, are given in the **Data Sheets** (Table 23). Some of the compounds in this activity contain hydrogen atoms attatched to oxygen and nitrogen atoms. The chemical shifts for both N–**H** and O–**H** can be variable, the value depending on several factors. They are usually broad peaks.

The *shape* of the signal given by any particular hydrogen atom is related to the number of neighbouring hydrogen atoms on adjacent carbons, as summarised in Table 1. This rule does not always apply to hydrogen atoms on oxygen or nitrogen.

Number of H atoms on adjacent C atoms	Shape of signal
0	single peak – singlet
1	two close peaks – doublet
2	three close peaks – triplet
3	four close peaks – quartet

Table 1 Shape of n.m.r. signal in relation to the number of neighbouring hydrogen atoms on adjacent carbon atoms. These splittings are only seen clearly in high resolution spectra.

What you do

Part 1: N.m.r. spectra of simple organic compounds

a Figures 1, 2 and 3 show the ^{1}H (proton) n.m.r. spectra of ethanol, ethanal and ethanoic acid respectively.

i Draw the full structural formula of each of these molecules.

ii Identify the hydrogen atoms responsible for each of the signals in the spectra.

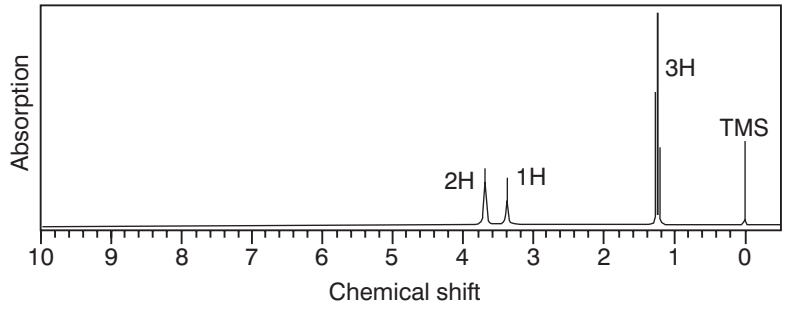


Figure 1 The n.m.r. spectrum of ethanol

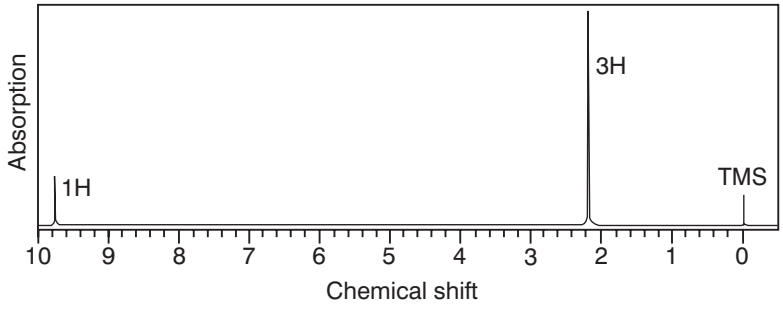


Figure 2 The n.m.r. spectrum of ethanal

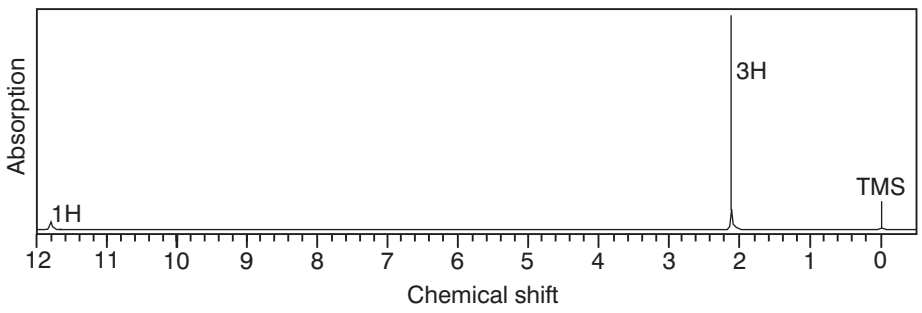


Figure 3 The n.m.r. spectrum of ethanoic acid

b Figures 4–7 show the n.m.r. spectra of propan-1-ol, propanal, propanone and propanoic acid, but not necessarily in this order.

i Draw the full structural formula of each of these molecules.

ii Identify, with reasons, which of the spectra, labelled A, B, C, D in Figures 4–7, corresponds to each of the structures you have drawn.

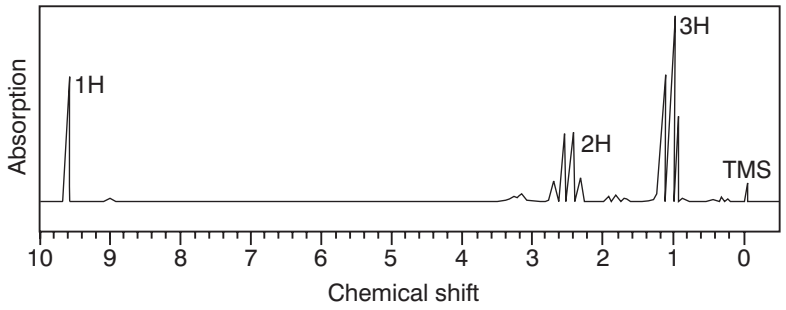


Figure 4 The n.m.r. spectrum A

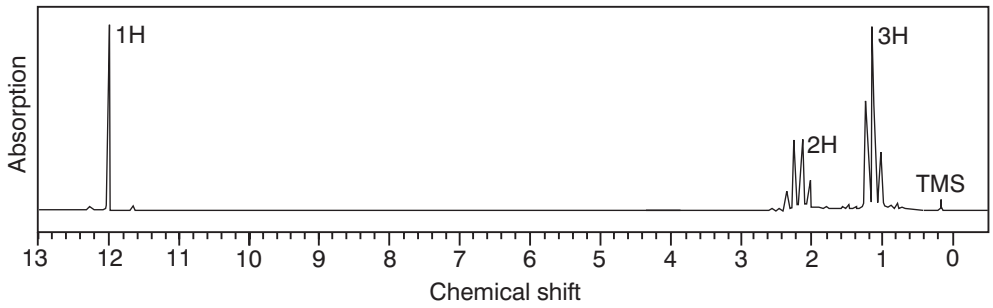


Figure 5 The n.m.r. spectrum B

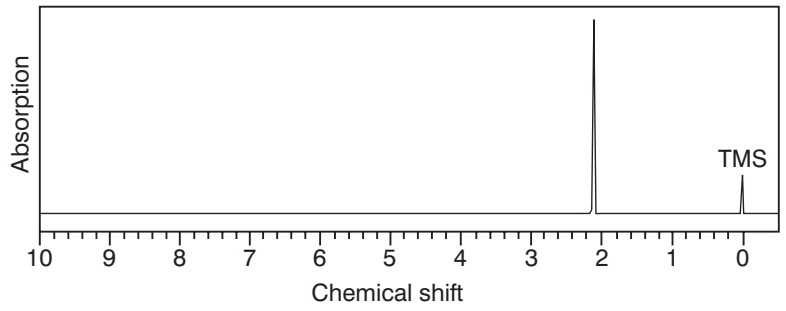


Figure 6 The n.m.r. spectrum C

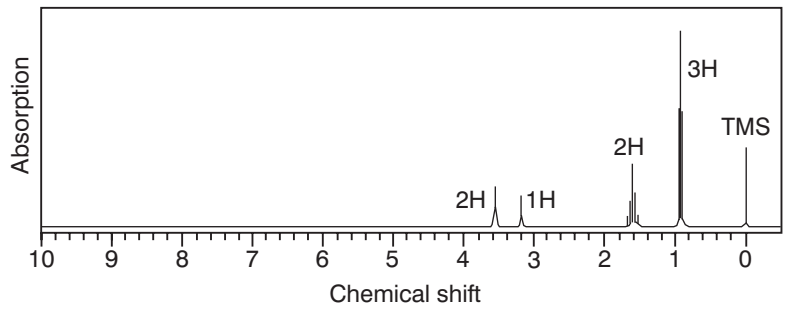


Figure 7 The n.m.r. spectrum D

c Figures 8, 9 and 10 show the n.m.r. spectra of aminoethane, 1-aminopropane and propanamide respectively.

i Draw the full structural formula of each of these molecules.

ii Identify the hydrogen atoms responsible for each of the signals in the n.m.r. spectra and, where possible, comment on the shape of these signals.

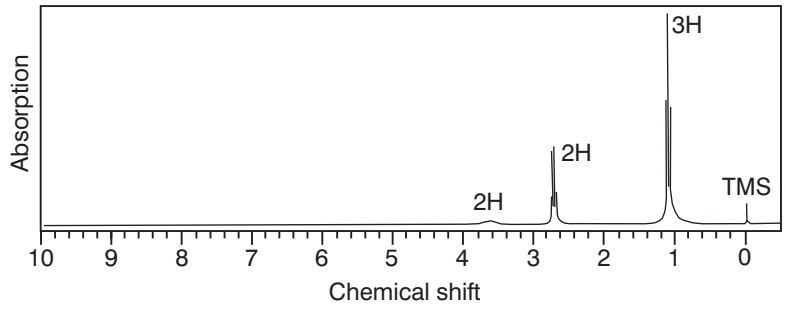


Figure 8 The n.m.r. spectrum of aminoethane

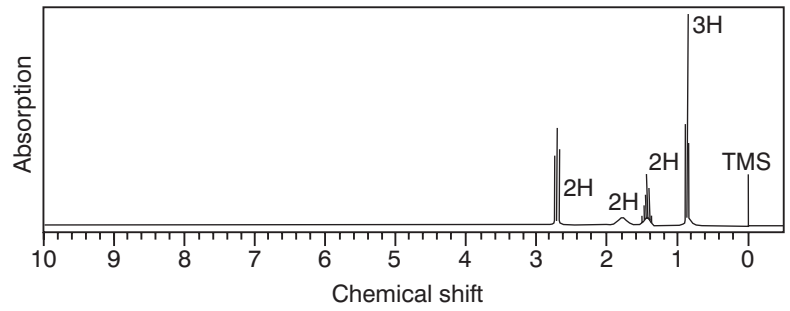


Figure 9 The n.m.r. spectrum of 1-aminopropane

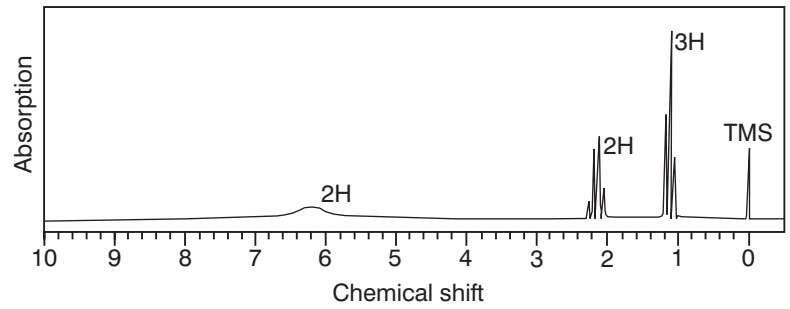
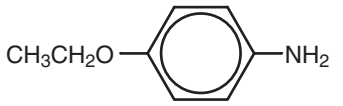


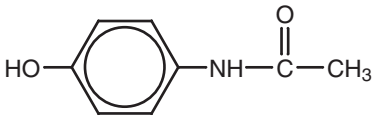
Figure 10 The n.m.r. spectrum of propanamide

Part 2: N.m.r. spectra of other nitrogen-containing compounds

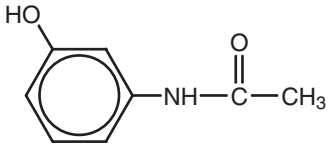
d Use the information provided in the **Data Sheets**, together with your knowledge of n.m.r. spectra in Part 1 to match the following structures 1–3 with the n.m.r. spectra E–G in Figures 11–13.



1



2



3

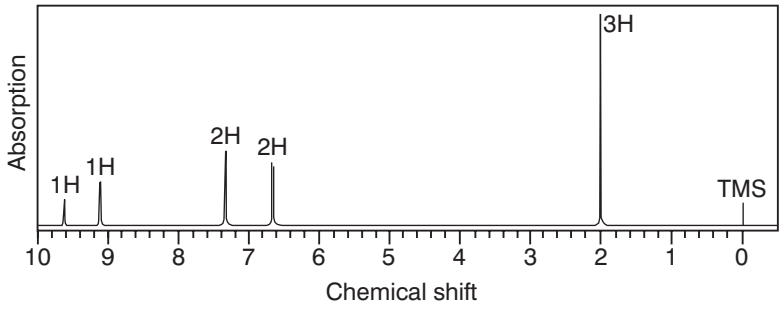


Figure 11 The n.m.r. spectrum E

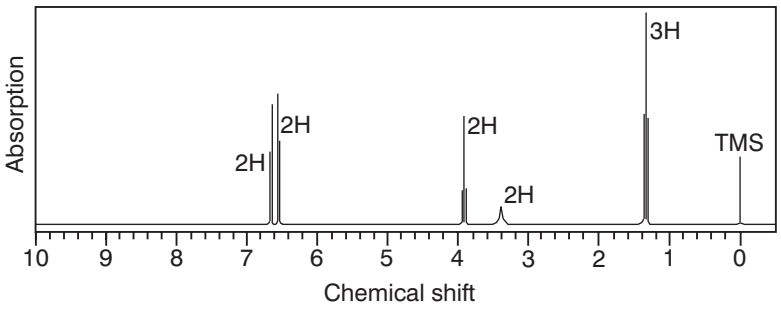


Figure 12 The n.m.r. spectrum F

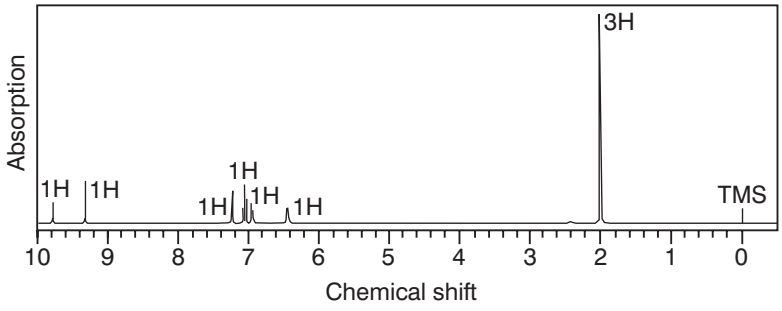


Figure 13 The n.m.r. spectrum G

e For the analgesic paracetamol, structure 2, use the information in the **Data Sheets** to predict the main features of its i.r. spectrum.

EP2.4

The shapes of α-amino acids

This activity reinforces your reading of* Chemical Ideas 3.3 *and* 3.6 *on the shapes of molecules and optical isomerism.

Requirements

- molecular model kit
- molecular modelling software (optional)

What you do

1 Draw a full structural formula for glycine. Mark on it the values you would expect for the bond angles.

2 Draw full structural formulae for the following amino acid –R groups, showing clearly any lone pairs. Mark on each structure the values you would expect for the bond angles.
a valine **b** serine **c** methionine **d** aspartic acid.

3 Build models of the structures in steps **1** and **2**. Check that the bond angles you predicted were correct, and see how the representations of the structures on flat pieces of paper compare with their three-dimensional shapes.

4 Build a simplified model of a general α-amino acid by using:
- a hydrogen atom for hydrogen
- a carbon atom for the –R group
- an oxygen atom for the –COOH group
- a nitrogen atom for the $-NH_2$ group.

You now have a central carbon atom surrounded by four different groups. Each group (–H, –R, –COOH and $-NH_2$) is represented by a different coloured atom. (This removes some of the 'clutter' of bulky groups so that you can see the arrangement round the central carbon atom clearly.)

Build a second model which is the mirror image of the model you have just built. Confirm to yourself that the two structures represent **enantiomers** (optical isomers).

5 Stand your two models from step **4** so that the H atoms point upwards. Look down each one from the H atom towards the central carbon atom. One enantiomer will have the sequence
COOH, **R**, **N**H_2 (CORN)
in a clockwise direction. This is the **L-amino acid**, the configuration that occurs in proteins. The other structure corresponds to the **D-amino acid**; D-amino acids occur in some bacterial peptides.

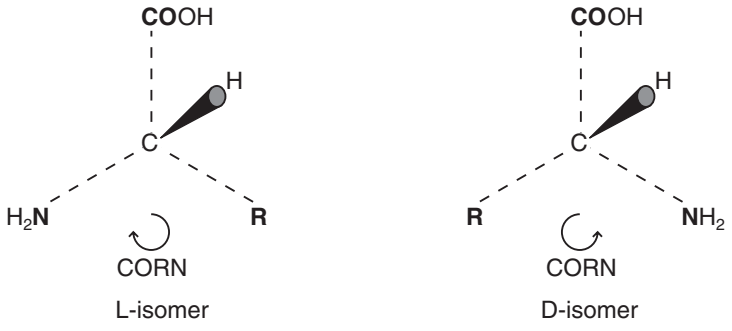


Figure 1 Looking down the H–C bond from hydrogen towards the central carbon atom

6 Replace the –R groups of your amino acid structures with H atoms, so that you have two models of glycine. Confirm that optical isomerism is no longer possible without four different groups around the central atom.

EP2.5

A testing smell

This activity makes use of a naturally occurring pair of enantiomers to illustrate how optical isomers can have different properties.

Requirements

- spearmint chewing gum (a half of a piece)
- caraway seeds, crushed (about 20)
- test-tubes wrapped in foil or paper to obscure their contents
- stoppers or clingfilm

What you do

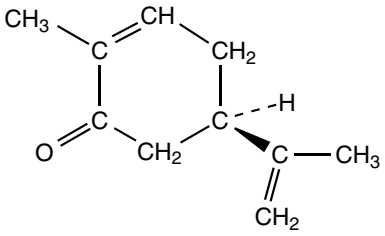
1 Label the test-tubes and their stoppers X, Y and Z. Place about a quarter of a piece of chewing gum into one of the tubes, and about 10 caraway seeds into another. Make sure you keep a record of which material goes into which tube.

2 Then place either another piece of chewing gum or another 10 caraway seeds into the third tube. Seal all three tubes with the correct stoppers.

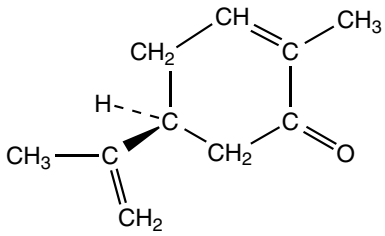
3 Get other members of your group to close their eyes and smell the contents of each tube in turn, telling you which tubes smell the same and which is different.

What it means

The principal smell of chewing gum is due to L-carvone which smells of spearmint. Caraway seeds smell of the enantiomer, D-carvone. It is claimed that about 20% of people cannot distinguish between these two smells.



L-carvone



D-carvone

QUESTIONS

a Which two functional groups are present in carvone?

b **i** Draw skeletal formulae for D- and L-carvone.
ii On your skeletal formulae, use an asterisk (*) to denote the chiral carbon atom.

c **i** What is the molecular formula of carvone?
ii Write down the molecular formula of the product of the reaction of D-carvone with bromine molecules, $Br_2(l)$.
iii Would you expect L-carvone to react in the same way with bromine? Explain your answer.
iv Draw a skeletal formula for the product of the reaction in **c ii**.
v How many chiral carbon atoms are there in the structure in **c iv**? Mark each one with an asterisk.

d D- and L-carvone are different in the way they smell to the majority of people. Suggest a reason why the enantiomers produce different responses from the smell receptors in the body.

e Work out the percentage of people in your class survey who fail to detect a difference between the two forms of carvone. How does your result compare with the figure of 20% quoted earlier in this activity? Comment on the fairness of the comparison.

EP2.6

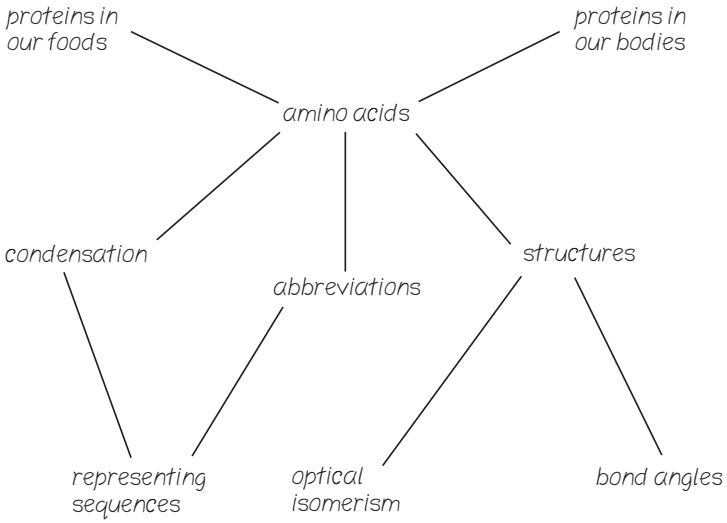
Taking note of proteins

***This activity will help you summarise the information in the first part of* Storyline EP2.**

Making a summary

Very early in this course, in the unit **The Elements of Life**, you probably carried out an activity – 'Making the most of your study of chemistry' (**Activity EL2.2**) – about recording information. This introduced the idea of writing 'branched notes'.

Below is the basis of some branched notes on amino acids and proteins. Each of the points needs to be branched out further with more information. Add the branches you think are necessary, and so build up a summary of the work you have done so far in **Storyline EP2**.



EP2.7

Modelling DNA

The double-helix arrangement of DNA can be explained in terms of intermolecular forces. This activity helps you work out these explanations, and become more familiar with the DNA structure.

Requirements

- molecular model kit
- plastic-coated wire, e.g. RS30 × 0.25 mm strand (1 m)
- plastic pegs, eg Cochrane's 'Minit' peg, type a (30)
- plastic straws to fit pegs, 10 cm (15)
- RASMOL molecular visualisation application and files of nucleic acid structures (optional)

Base pairing

1 Refer to **Storyline EP2** and use a molecular model kit to build models of the structures of the four bases in DNA. Leave spare bonds to indicate the connections to the sugar–phosphate 'backbone'.

2 Try different combinations of pairs of bases to investigate which molecules form strong hydrogen bonds with one another. Remember:
- the bonds to the sugar–phosphate 'backbone' must be at opposite sides of the bases
- the hydrogen bonds should be about 50% longer than the covalent bonds
- the bases interact in a flat arrangement.

3 Draw diagrams for the structures of the base pairs which fit well together.

The double helix

4 Use the plastic-coated wire, plastic straws and pegs supplied to make a ladder like the one shown in Figure 1. Use about 15 pegs on each side.

a What feature of DNA is represented by:
- **i** the plastic-coated wire?
- **ii** the straws?

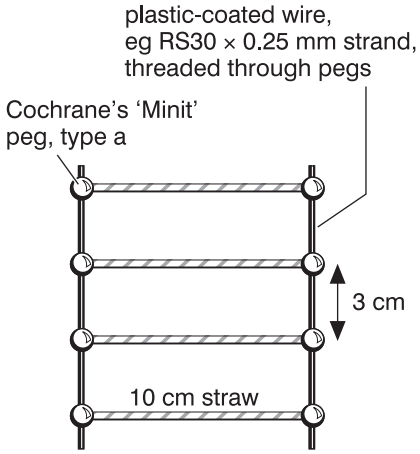


Figure 1 Building a double helix

5 Twist your model to form a double helix with ten straws to a turn – that is the *eleventh* straw should lie directly over the *first* straw. This represents the extent to which DNA is twisted.

6 Compare your model with the space-filling representation of DNA shown in Figure 2.

7 You might take the opportunity to investigate the DNA structure further by using a molecular visualisation package (eg RASMOL).

b What do you notice about the region in the centre of the double helix – the region occupied by the bases? (These are shown as unshaded atoms in the figure.)

c Explain why the DNA double helix could not be twisted more tightly than it is.

d As you have seen, hydrogen bonding is responsible for the interactions between the bases in a direction *across* the axis of the double helix – in other words, horizontally in Figure 2. Explain what type of intermolecular bonding is responsible for the interactions between the bases *along* the axis of the double helix – in other words, vertically in Figure 2.

e Your answer to **d** should help you to understand why the DNA double helix is twisted to the extent shown by your model. Explain why a *less* tightly twisted DNA double helix would be unlikely to form.

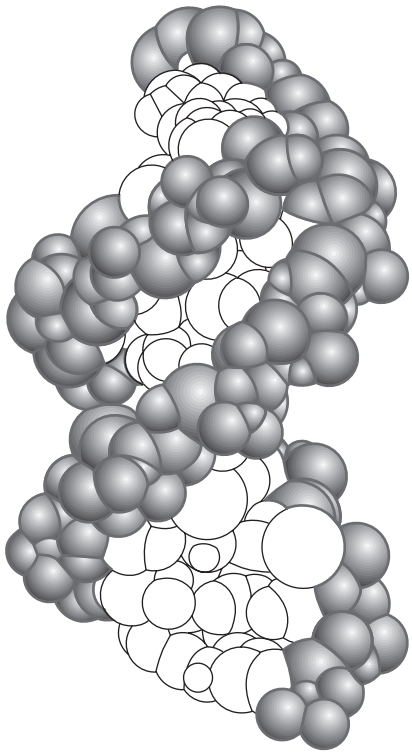


Figure 2 Space-filling model of DNA

EP2.8

Life reveals its twisted secret

This activity will give you practice at composing a piece of scientific writing from a range of source materials.

What you do

Imagine that it is 1953. Francis Crick and James Watson have just announced a momentous discovery about the structure of DNA. You have been commissioned to write an article of 400–500 words for a science magazine. Your article should review the various structures which have been proposed for DNA, and explain why the Crick-Watson structure seems most appropriate.

To help you, you have collected together some clippings from books and magazines, and some brief details about the principal research scientists in the field. You may include illustrations in your article. Remember – your audience will have some understanding of science, though they will not be experts in this particular field.

When you have finished, write a short abstract (no more than 50 words) which summarises the main points of your article.

Setting the scene

By the early 1950s, protein structure had been well worked out. Several groups were turning their attention to DNA, the one remaining cell polymer with an unknown structure.

The following people were foremost among those involved.

Maurice Wilkins

He was a respected physicist working at King's College, London. He had decided to tackle the DNA structure using X-ray diffraction as his research technique. At a conference in Naples in Spring 1951 he showed a slide of the X-ray diffraction pattern of DNA which, in spite of Wilkins' dry delivery, excited James Watson to the possibilities of X-ray study of the molecule.

James Watson

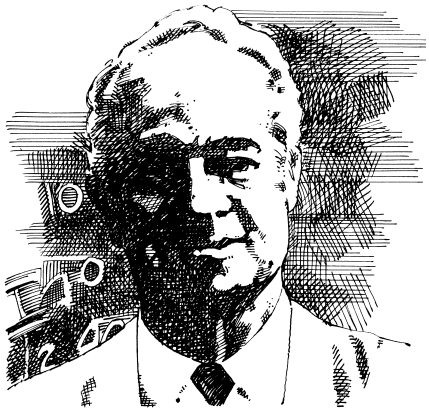
A young fun-loving American biologist who came to Cambridge in 1951 to pursue his hunch that X-ray diffraction was the clue to understanding the structure of macromolecules. He joined the Cavendish laboratory in a group working on protein structure, but his thoughts were always turning to DNA.

Rosalind Franklin

She was a young, brilliant X-ray crystallographer, and an ardent feminist, who also worked at King's College, London. Called in by Wilkins to assist with his DNA work, she soon became an equal partner in the research.

Linus Pauling

He was a very successful and established chemist working at the California Institute of Science and Technology (Cal Tech). He had recently discovered (with Robert Corey) the α-helical structure for proteins. This he revealed in a lecture with a distinct 'show business' flair, proudly unveiling his model with a flourish near the end of the lecture.



Francis Crick

A maverick English physicist who had worked on magnetic mines in the Second World War. He was supposed to be researching for a PhD in the Cavendish group which Watson joined. In practice, though, he was constantly picking up and attempting to improve the ideas of others, and he too had his sights set on the DNA structure.

The clippings

Rosalind Franklin's early ideas about DNA (November 1951)

The general characteristics of the diagram suggest that the DNA chains are in a helical form.

… The results suggest a helical structure (which must be very closely packed) containing probably 2, 3 or 4 co-axial nucleic acid chains per helical unit, *and having the phosphate groups near the outside*.

A. Sayre 1975. *Rosalind Franklin and DNA* (New York: Norton, pp. 125–6). Reprinted 1978.

Crick and Watson's 3-chain model (1951/1952)

Decisions had to be made about the number of polynucleotide chains within the DNA molecule. Superficially, the X-ray data were compatible with two, three, or four strands. It was all a question of the angle and radii at which the DNA strands twisted about the central axis.

… we had decided upon models in which the sugar-phosphate backbone was in the center of the molecule.

… we looked at the pros and cons of one, two, three, and four chains, quickly dismissing one-chain helices as incompatible with the evidence in our hands. As to the forces that held the chains together, the best guess seemed to be salt bridges in which divalent cations like Mg^{++} held together two or more phosphate groups. Admittedly there was no evidence that Rosy's samples contained any divalent ions, and so we might be sticking our necks out. … with luck, the addition of magnesium or possibly calcium ions to the sugar-phosphate backbone would quickly generate an elegant structure, the correctness of which would not be debatable.

… a shape began to emerge which brought back our spirits. Three chains twisted about each other in a way that gave rise to crystallographic repeat every 28 Å along the helical axis.

James D. Watson 1968. *The Double Helix* (London: Weidenfeld & Nicolson, pp. 77–89). With new introduction, 1999 (London: Penguin Books).

Note: An ångström (Å) is 1×10^{-10} m, so 28 Å is 2.8 nm.

Franklin's response to the Crick-Watson 3-chain model (1952)

Wilkins was invited to Cambridge to witness the triumph; William Seeds, who worked with Wilkins, came along, and Rosalind and Gosling as well. The session was opened by Crick with an exposition of helical diffraction theory, a subject upon which he was very expert, and went on to a description of the model, of which Rosalind plainly did not think much. Her disdain of it Watson accounts for on the grounds that what was proposed was a helical structure, while Rosalind did not admit that a shred of evidence existed to indicate that DNA was helical – a curious statement, considering that very shortly before she had presented a good deal of evidence suggesting that the B form of DNA was exactly that. What she did object to in the proposed structure – and aggressively, we are told – was that the three-chain model had its phosphate groups held together by Mg^{++} ions in a way she thought unlikely, considering that by her calculations the Mg^{++} ions would be surrounded by tight shells of water molecules.

And as Watson was required to confess, her objections, though very annoying, were not mere perversity.

A. Sayre 1975. *Rosalind Franklin and DNA* (New York: Norton, pp. 135–6). Reprinted 1978.

Pauling's 3-helix model (1952/1953)

We have formulated a structure for the nucleic acids which is compatible with the main features of the X-ray diagram and with the general principles of molecular structure, and which accounts satisfactorily for some of the chemical properties of the substances. The structure involves three intertwined helical polynucleotide chains. Each chain, which is formed by phosphate di-ester groups and linking β-D-ribofuranose [D-ribose] or β-D-deoxyribofuranose [D-deoxyribose] residues with 3', 5' linkages, has approximately twenty-four nucleotide residues in seven turns of the helix. The helixes have the sense of a right handed screw. The phosphate groups are closely packed about the axis of the molecule, with the pentose residues surrounding them, and the purine and pyrimidine groups projecting radially, their planes being approximately perpendicular to the molecular axis. The operation that converts one residue to the next residue in the polynucleotide chain is rotation by about 105° and translation by 3.4 Å.

A detailed description of the structure is appearing in the February 1953 issue of the *Proceedings of the National Academy of Sciences of the United States of America*.

Linus Pauling, Robert B. Corey 1953. Structure of the Nucleic Acids. In *Nature*, February 21, vol. 171, p.346.

Watson's response to Pauling's ideas (1953)

At once I felt something was not right. I could not pinpoint the mistake, however, until I looked at the illustrations for several minutes. Then I realized that the phosphate groups in Linus' model were not ionized, but that each group contained a bound hydrogen atom and so had no net charge. Pauling's nucleic acid in a sense was not an acid at all. Moreover, the uncharged phosphate groups were not incidental features. The hydrogens were part of the hydrogen bonds that held together the three intertwined chains. Without the hydrogen atoms, the chains would immediately fly apart and the structure vanish.

Everything I knew about nucleic-acid chemistry indicated that phosphate groups never contained bound hydrogen atoms.

James D. Watson 1968. *The Double Helix* (London: Weidenfeld & Nicolson, p. 160). With new introduction, 1999 (London: Penguin Books).

Pauling's later comments

I calculated the number of polynucleotide chains per unit to be exactly three. This result surprised me, because I had expected the value 2 if the nucleic acid fibres really represented genes … During the next month I strove to find a way of arranging the polynucleotide chains in a triple helix, and was successful, although the structure was described as "an extraordinarily tight one, with little opportunity for change in positions of the atoms" …

In hindsight, it is evident that I made a mistake … in having decided to study the triple helix rather than the double helix. … I am now astonished that I began work on the triple helix structure, rather than on the double helix. I had not forgotten … that the gene might consist of two complementary molecules, but for some reason, not clear to me now, the triple chain structure apparently appealed to me, possibly because the assumption of a three-fold axis simplified the search for an acceptable structure.

Linus Pauling 1974. Molecular Basis of Biological Specificity. In *Nature*, vol. 248, p. 771.

Crick and Watson's crucial paper

They acknowledge the contribution of Rosalind Franklin and Maurice Wilkins at the end of the paper. (See next sheet.)

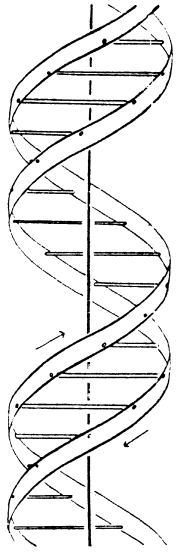
MOLECULAR STRUCTURE OF NUCLEIC ACIDS

A Structure for Deoxyribose Nucleic Acid

WE wish to suggest a structure for the salt of deoxyribose nucleic acid (D.N.A). This structure has novel features which are of considerable biological interest.

A structure for nucleic acid has already been proposed by Pauling and Corey[1]. They kindly made their manuscript available to us in advance of publication. Their model consists of three intertwined chains, with the phosphates near the fibre axis, and the bases on the outside. In our opinion, this structure is unsatisfactory for two reasons: (1) We believe that the material which gives the X-ray diagrams is the salt, not the free acid. Without the acidic hydrogen atoms it is not clear what forces would hold the structure together, especially as the negatively charged phosphates near the axis will repel each other. (2) Some of the van der Waals distances appear to be too small.

Another three-chain structure has also been suggested by Fraser (in the press). In his model the phosphates are on the outside and the bases on the inside, linked together by hydrogen bonds. This structure as described is rather ill-defined, and for this reason we shall not comment on it.



This figure is purely diagrammatic. The two ribbons symbolize the two phosphate—sugar chains, and the horizontal rods the pairs of bases holding the chains together. The vertical line marks the fibre axis.

We wish to put forward a radically different structure for the salt of deoxyribose nucleic acid. This structure has two helical chains each coiled round the same axis (see diagram). We have made the usual chemical assumptions, namely, that each chain consists of phosphate diester groups joining ß-D-deoxyribofuranose residues with 3',5' linkages. The two chains (but not their bases) are related by a dyad perpendicular to the fibre axis. Both chains follow right-handed helices, but owing to the dyad the sequences of the atoms in the two chains run in opposite directions. Each chain loosely resembles Furberg's[2] model No. 1; that is, the bases are on the inside of the helix and the phosphates on the outside. The configuration of the sugar and the atoms near it is close to Furberg's 'standard configuration', the sugar being roughly perpendicular to the attached base. There is a residue on each chain every 3·4 A. in the z-direction. We have assumed an angle of 36° between adjacent residues in the same chain, so that the structure repeats after 10 residues on each chain, that is, after 34 A. The distance of a phosphorus atom from the fibre axis is 10 A. As the phosphates are on the outside, cations have easy access to them.

The structure is an open one, and its water content is rather high. At lower water contents we would expect the bases to tilt so that the structure could become more compact.

The novel feature of the structure is the manner in which the two chains are held together by the purine and pyrimidine bases. The planes of the bases are perpendicular to the fibre axis. They are joined together in pairs, a single base from one chain being hydrogen-bonded to a single base from the other chain, so that the two lie side by side with identical z-co-ordinates. One of the pair must be a purine and the other a pyrimidine for bonding to occur. The hydrogen bonds are made as follows: purine position 1 to pyrimidine position 1; purine position 6 to pyramidine position 6.

If it is assumed that the bases only occur in the structure in the most plausible tautomeric forms (that is, with the keto rather than the enol configurations) it is found that only specific pairs of bases can bond together. These pairs are: adenine (purine) with thymine (pyrimidine), and guanine (purine) with cytosine (pyrimidine).

In other words, if an adenine forms one member of a pair, on either chain, then on these assumptions the other member must be thymine; similarly for guanine and cytosine. The sequence of bases on a single chain does not appear to be restricted in any way. However, if only specific pairs of bases can be formed, it follows that if the sequence of bases on one chain is given, then the sequence on the other chain is automatically determined.

It has been found experimentally[3,4] that the ratio of the amounts of adenine to thymine, and the ratio of guanine to cytosine, are always very close to unity for deoxyribose nucleic acid.

It is probably impossible to build this structure with a ribose sugar in place of the deoxyribose, as the extra oxygen atom would make too close a van der Waals contact.

The previously published X-ray data[5,6] on deoxyribose nucleic acid are insufficient for a rigorous test of our structure. So far as we can tell, it is roughly compatible with the experimental data, but it must be regarded as unproved until it has been checked against more exact results. Some of these are given in the following communications. We were not aware of the details of the results presented there when we devised our structure, which rests mainly though not entirely on published experimental data and stereochemical arguments.

It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material.

Full details of the structure, including the conditions assumed in building it, together with a set of co-ordinates for the atoms, will be published elsewhere.

We are much indebted to Dr. Jerry Donohue for constant advice and criticism, especially on interatomic distances. We have also been stimulated by a knowledge of the general nature of the unpublished experimental results and ideas of Dr. M. H. F. Wilkins, Dr. R. E. Franklin and their co-workers at King's College, London. One of us (J. D. W.) has been aided by a fellowship from the National Foundation for Infantile Paralysis.

J. D. Watson
F. H. C. Crick

Medical Research Council Unit for the Study of the Molecular Structure of Biological Systems.
Cavendish Laboratory, Cambridge.
April 2.

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NATURE

NO. 4356 April 25, 1953

EP6.1

Testing for glucose

Diabetes can be diagnosed by detecting glucose in the urine. The test must be specific to avoid confusion with other compounds which may be present. The specificity of an enzyme in its reaction with a particular substrate is therefore a useful basis for such a test. In this activity you can find out about the specificity of the enzyme glucose oxidase and investigate some of its other properties.

Requirements

- glucose test strips (such as Clinistix™ or Diastix™)
- hydrochloric acid, 1 mol dm^{-3}
- sodium hydroxide solution, 1 mol dm^{-3}
- glucose solution, 0.02 mol dm^{-3}
- solutions or samples of other sugars

sodium hydroxide solution

IRRITANT

CARE Eye protection must be worn.

WEAR EYE PROTECTION

What you do

Carefully read the instructions which come with the glucose test strips, and make sure you know how they work (see also **Storyline EP6**).

1 The glucose solution you are supplied with has a similar concentration to the glucose in the urine of someone who is diabetic. Check that the test strips work with the glucose solution.

2 Investigate how the activity of the enzyme *glucose oxidase* is affected by changing:

- pH
- temperature
- substrate (the sugar used).

Record your results in the form of a table.

3 You might like to go on to refine your experiments in order to discover in more detail how the enzyme's activity depends on pH and temperature.

4 Summarise your findings and suggest explanations for the effects you have noted.

EP6.2

Succinate dehydrogenase (Optional extension)

In this activity you will use models to investigate the binding of a substrate to the active site of an enzyme. This will help you to understand why enzymes are so specific, and how some compounds can act as enzyme inhibitors.

Requirements

- molecular model kit

Introduction

Butanedioic acid (succinic acid) is oxidised to *trans*-butenedioic acid by removal of hydrogen. This reaction is catalysed by the enzyme *succinate dehydrogenase*.

$$\underset{\text{butanedioic acid}}{HOOC–CH_2–CH_2–COOH} \rightarrow \underset{\textit{trans}\text{-butenedioic acid}}{HOOC–CH=CH–COOH}$$

The enzyme is *inhibited* by propanedioic acid: $HOOC–CH_2–COOH$; in other words, its catalytic activity is less in the presence of propanedioic acid. This, together with other evidence, suggests that *two* –COOH groups are involved in binding the substrate to the active site.

The action of the enzyme is summarised in Figure 1.

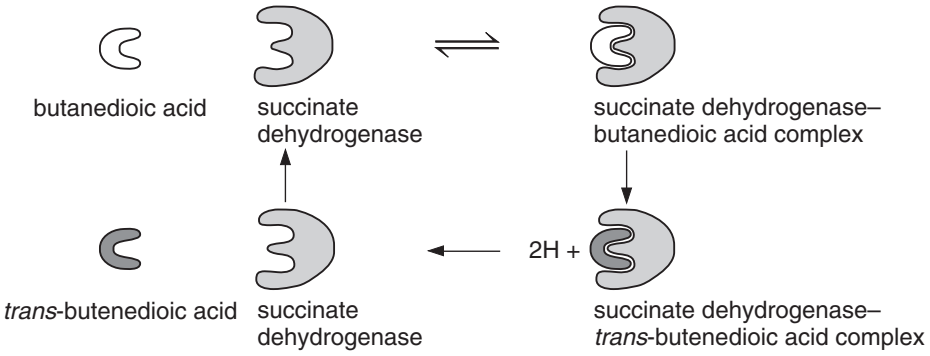


Figure 1 The action of succinate dehydrogenase

What you do

1 Make molecular models of the three acids (butanedioic acid, *trans*-butenedioic acid, and propanedioic acid).

2 Place the molecule of *trans*-butenedioic acid on a piece of paper so that all the atoms are touching the paper. Draw circles on the paper to mark the positions of the oxygen and hydrogen atoms of the –COOH groups. Note the position of the other hydrogen atoms. (Remember, this is the product of the oxidation reaction.)

3 Now manipulate your structure of butanedioic acid so that the hydrogens and oxygens of its –COOH groups can be placed on the same marks. One H atom of each $–CH_2–$ group should also be touching the paper. Note the positions of the other two H atoms – the ones which are removed by the enzyme.

4 Leave the model of butanedioic acid in place and superimpose your model of propanedioic acid on it so that the –COOH groups coincide. (You will need to 'close up' the butanedioic acid structure a little to achieve this.) Using a different colour, mark the new positions of the oxygen and hydrogen atoms of the –COOH groups.

This should show you that both butanedioic acid and propanedioic acid can be bound by their –COOH groups to the same site on the enzyme. The product of the oxidation reaction, *trans*-butenedioic acid, binds to this site less well and is released from the enzyme.

The oxidation (removal of hydrogen) occurs at another part of the active site. This must be where the C–C bond between the two central carbons of butanedioic acid naturally comes when it is placed as above.

Propanedioic acid is an inhibitor because it has no C–C bond to oxidise, but it can bind onto the site and block it.

5 Now consider pentanedioic acid: $HOOC–CH_2–CH_2–CH_2–COOH$.

Make a model of its structure. Try to fit it onto the marks you made in **4**. Decide whether you would expect it to:

- bind to the enzyme or not
- be oxidised by the enzyme to $HOOC–CH_2–CH=CH–COOH$
- be an inhibitor.

EP6.3

The effect of enzyme and substrate concentrations on the rate of a reaction

In this activity you will follow the progress of a catalysed reaction by measuring the volume of gas produced as the reaction proceeds. You will use the initial rates of a series of experiments to find the orders of the reaction with respect to enzyme and substrate.

Requirements

- burette (50 cm^3)
- trough or bowl
- boiling tube with bung and delivery tube
- graduated pipette (5 cm^3) and safety filler
- measuring cylinder (10 cm^3)
- hydrogen peroxide solution, 5 vol (25 cm^3)
- yeast suspension (20 cm^3), made from 2 g dried yeast in 160 cm^3 water aerated for several hours
- stopwatch

CARE Eye protection must be worn.

Introduction

In this activity, the substrate is *hydrogen peroxide* (H_2O_2) and the enzyme is *catalase*. You will use yeast as a source of catalase.

Hydrogen peroxide is formed as a waste product of metabolism by many organisms. It is toxic and must be rapidly removed from the cells. The enzyme catalase catalyses the decomposition of hydrogen peroxide to produce water and oxygen.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

The reaction can be monitored by measuring the volume of oxygen produced as the reaction proceeds, and plotting a graph of the volume of oxygen produced against time. You can find the rate of the reaction (in terms of the volume of oxygen produced per second) at any time by measuring the gradient of the curve.

You may like to practise your IT skills and make use of graph-plotting computer software to plot your results. It is usually best, however, to draw the best-fitting line or curve by hand.

It is important when investigating rates of reaction to vary one factor at a time. All other factors which could affect the rate should be kept constant.

What you do

It will be best to work in groups. One group should tackle Part 1 while another group does Part 2. Combine your results at the end.

Take the opportunity to use a spreadsheet to collect your data. The graph-plotting function will help you to find the initial rate of each reaction.

Part 1: Varying the concentration of hydrogen peroxide

1. Fill a burette with water and invert it in a trough of water. Hold it in place with a clamp and check that the burette is leak-proof. Make sure you leave enough room in the trough for water which will be displaced from the burette.
2. Place 2.5 cm^3 of well-stirred yeast suspension in a boiling tube and set up the apparatus in Figure 1. *Carefully* open the tap on the burette until the meniscus falls to the 50 cm^3 mark (i.e. zero for this experiment as the burette is upside down).
3. Measure out 5 cm^3 of hydrogen peroxide in a 10 cm^3 measuring cylinder. Organise yourselves for taking and recording readings of volume at 10-second intervals for 4 minutes.

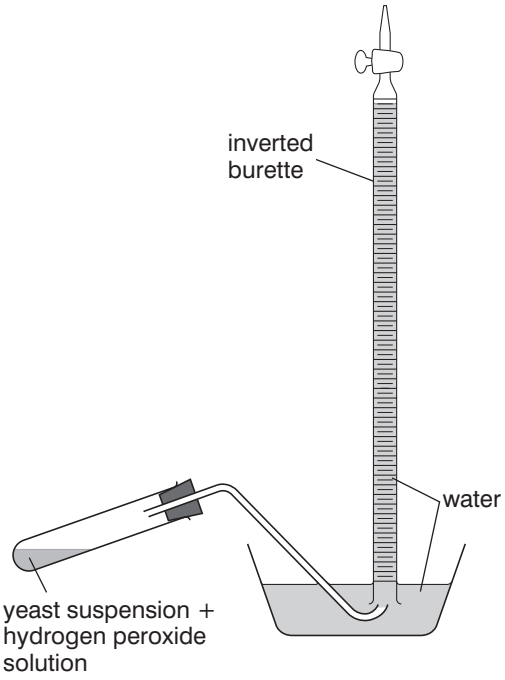


Figure 1 Measuring the volume of oxygen produced

4 Add 5 cm^3 of hydrogen peroxide to the yeast suspension and *quickly* replace the bung. Zero time is counted as the time the first bubble appears in the burette. Take a reading of the volume of gas in the burette every 10 seconds for 4 minutes.

5 Wash out the boiling tube, refill the burette, and repeat steps **1**–**4** four more times, using:

$4\,cm^3\ H_2O_2 + 1\,cm^3$ distilled H_2O
$3\,cm^3\ H_2O_2 + 2\,cm^3$ distilled H_2O
$2\,cm^3\ H_2O_2 + 3\,cm^3$ distilled H_2O
$1\,cm^3\ H_2O_2 + 4\,cm^3$ distilled H_2O

in the measuring cylinder. Everything else should be the same in each experiment.

6 Plot the volume of O_2 given off (vertical axis) against time (horizontal axis) for each experiment, drawing all the curves on the same axes.

QUESTIONS

a How does the rate of the reaction change as the reaction proceeds? Explain why the rate changes in this way.

b Draw a tangent to each curve at $t = 0$. This represents the *initial rate* of the reaction: its rate at the start. How does the initial rate of the reaction vary with the starting concentration of hydrogen peroxide?

c Measure the gradient of each tangent. Plot the initial rate for each experiment against the volume of hydrogen peroxide used. (The volume of hydrogen peroxide is proportional to its concentration since the total volume is kept constant.) What is the order of the reaction with respect to hydrogen peroxide?

Part 2: Varying the concentration of enzyme

7 Follow the procedure in steps **1**–**4** in Part 1.

8 Wash out the boiling tube, refill the burette, and repeat steps **1**–**4** four more times, using:

$2.0\,cm^3$ yeast + $0.5\,cm^3$ distilled H_2O
$1.5\,cm^3$ yeast + $1.0\,cm^3$ distilled H_2O
$1.0\,cm^3$ yeast + $1.5\,cm^3$ distilled H_2O
$0.5\,cm^3$ yeast + $2.0\,cm^3$ distilled H_2O

in the boiling tube. Everything else should be the same in each experiment.

9 Plot the volume of O_2 given off (vertical axis) against time (horizontal axis) for each experiment, drawing all the curves on the same axes.

QUESTIONS

d How does the rate of the reaction change as the reaction proceeds? Explain why the rate changes in this way.

e Draw a tangent to each curve at $t = 0$. This represents the *initial rate* of the reaction: its rate at the start. How does the initial rate of the reaction vary with the starting concentration of the enzyme? You can assume that the starting concentration of the enzyme is proportional to the volume of yeast used, since the total volume was kept constant.

f Measure the gradient of each tangent. Plot the initial rate for each experiment against the volume of yeast used. What is the order of the reaction with respect to the enzyme?

EP6.4

Using the iodine clock method to find the order of a reaction

This activity illustrates another way in which the initial rate method can be used to determine the order of a reaction with respect to one of the reactants.

Requirements

- 0–110 °C thermometer
- boiling tubes (5)
- test-tubes
- burettes (or graduated pipettes 1 cm^3, 2 cm^3 and 5 cm^3)
- potassium iodide solution, 1.00 mol dm^{-3} (15 cm^3)
- potassium peroxodisulphate(VI) ($K_2S_2O_8$) solution, 0.0400 mol dm^{-3} (10 cm^3)
- sodium thiosulphate ($Na_2S_2O_3$) solution, 0.0100 mol dm^{-3} (10 cm^3)
- freshly made starch solution (5 cm^3)
- stopwatch

potassium peroxodisulphate(VI) solution

CARE Eye protection must be worn.

About the reaction

Peroxodisulphate(VI) ions and iodide ions react together in solution to form sulphate(VI) ions and iodine.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

Both reactants and the sulphate ions are colourless, so the progress of the reaction can be measured by following the colour of the iodine produced. The iodine can be detected even more clearly by placing some starch in the reaction mixture: iodine forms an intense blue-black complex with starch.

One way of measuring the *initial rate* of the reaction is to measure how long the reaction takes to produce a small, fixed amount of iodine. By answering the questions which accompany this activity, you can work out what amount of iodine has been chosen here, and what fraction of the extent of reaction this represents.

You can make the time taken to produce a particular amount of iodine really obvious if you add thiosulphate ions to the reaction mixture at the start. Thiosulphate ions turn iodine back to iodide ions.

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

So, no starch-iodine colour will appear until all the thiosulphate has been used up. What you see is a colourless reaction mixture sitting there as though nothing is happening; then, suddenly, it turns blue. If you measure how long that takes, you know how long it took to use up all the thiosulphate and, therefore, how long it took to produce the equivalent amount of iodine.

This method of studying reaction rates is sometimes called the *clock method*, and this experiment is an example of an *iodine clock* experiment. You are going to use it to investigate how the reaction rate depends on the concentration of iodide ions in the reaction mixture.

You may like to practise your IT skills and make use of graph-plotting computer software to plot your results. It is usually best, however, to draw the best-fitting line or curve by hand.

What you do

1 First you are going to make up reaction mixture 1 from Table 1, and measure how long it takes for the blue iodine-starch colour to appear.

Look carefully at Table 1. The five mixtures differ only in the concentration of iodide ions. Water is added to keep the total volume of solution constant, so the concentration of everything else is the same in each mixture.

Reaction rates depend upon temperature. Measure the temperature of each experiment. Make sure that all your results are taken at approximately the same temperature and record an average value.

You can place the potassium iodide, sodium thiosulphate, starch and (for later mixtures) water straight into a boiling tube. You must measure out the potassium peroxodisulphate(VI) solution (**CARE** Harmful. Oxidiser) into a separate container, such as a test-tube.

2 When you are ready to start the experiment, pour the potassium peroxodisulphate(VI) solution into the mixture in the boiling tube. Immediately start timing, and carefully stir the reaction mixture with a thermometer to ensure that everything is properly mixed. Record the time taken for the blue colour to appear.

Mixture	Volume of KI(aq) /cm^3	Volume of water /cm^3	Volume of $Na_2S_2O_3$(aq) /cm^3	Volume of starch solution/cm^3	Volume of $K_2S_2O_8$(aq) /cm^3
1	5	0	2	1	2
2	4	1	2	1	2
3	3	2	2	1	2
4	2	3	2	1	2
5	1	4	2	1	2

Table 1 Mixtures for the iodine clock experiments

3 Repeat the procedure with mixtures 2–5, and record the time taken for the blue colour to appear in each case.

Find the order of reaction

You could use a spreadsheet to collect your results and to perform the calulations.

To find the order of the reaction with respect to iodide ions, you need to know how the initial rate of the reaction varies with iodide ion concentration. The steps in the calculation are summarised below:

- Work out $[I^-]$ in each mixture.
- Work out the amount of I_2 produced before the blue-black colour appears.
- Use this amount of I_2 and the clock time to work out the initial rate of reaction for each mixture.
- Plot a graph of the initial rate of reaction against $[I^-]$.
- Use the graph to determine the order of the reaction with respect to I^- ions.

The questions on the next sheet will help you work through these steps.

QUESTIONS

a Draw up a results table using the headings below:

Mixture	Concentration of I^-(aq)/mol dm^{-3}	Clock time /s	Rate /mol dm^{-3} s^{-1}	Temp /°C

Table 2 Results table

b Calculate values for the concentrations of iodide ions in the five reaction mixtures. Record these in the table, together with the corresponding times for the blue-black colour to appear (the clock times).

c Which reactant, I^- or $S_2O_8^{2-}$, is in excess in the reaction mixtures? The reactant *not* in excess will be used up in the reaction. It determines the total amount of iodine which can be produced.

d What is the total amount in moles of iodine which can be produced by each of the reaction mixtures?

e **i** What amount in moles of thiosulphate ions is added to each reaction mixture?
ii What amount of iodine will be used up by thiosulphate ions during the course of each experiment?
iii What percentage of the extent of reaction is studied during the experiments? (For the clock method to work well, the extent of reaction studied should be no more than 10–15% of the total extent of the reaction.)

f The initial rate of the reaction can be measured in mol dm^{-3} I_2 produced per second.
i For each mixture, divide your answer to **e ii** by the time taken for the appearance of the blue colour, and so calculate the initial rate (in mol dm^{-3} s^{-1}) at which each mixture reacts.
ii Record the reaction rates in the table.

g **i** Plot a graph of rate against concentration of iodide ions (horizontal axis).
ii What is the order of reaction with respect to iodide ions?

h A similar series of experiments shows that the reaction is first order with respect to $S_2O_8^{2-}$ ions.
i Write a rate equation for the reaction of peroxodisulphate(VI) ions and iodide ions.
ii What is the *overall* order of the reaction?
iii Calculate the rate constant for the reaction using the gradient of the graph you obtained in **g i**. Make sure you give the correct units and the temperature at which your measurements were made.

EP6.5

Enzyme kinetics

Accurate results in experiments involving enzymes can be hard to obtain. This activity provides you with two exercises, based on accurate data, which should help to reinforce your work about the rates of enzyme-catalysed reactions. Use* Storyline EP6 *to help you explain your results.

Introduction

The enzyme *urease* catalyses the hydrolysis of urea.

$$H_2N–CO–NH_2(aq) + H_2O(l) \rightarrow CO_2(aq) + 2NH_3(aq)$$

In the exercises which follow, the initial rate of reaction was measured by finding the number of moles of urea which had been hydrolysed during the first three minutes of the reaction. The average rate over the first three minutes, in units of mol dm^{-3} min^{-1}, was then found.

Exercise 1

The results described in Table 1 represent a series of experiments in which the concentration of urea (the substrate) was varied but the concentration of urease (the enzyme) was kept constant.

Concentration of urea/mol dm^{-3}	Rate/mol dm^{-3} min^{-1}
0	0
0.005	1.7×10^{-6}
0.010	2.3×10^{-6}
0.020	3.2×10^{-6}
0.050	4.4×10^{-6}
0.100	5.9×10^{-6}
0.200	7.2×10^{-6}
0.300	7.7×10^{-6}
0.400	8.0×10^{-6}
0.500	8.1×10^{-6}

Table 1

Plot a graph of the reaction rate against the substrate concentration (horizontal axis).

a When the substrate concentration is high, what is the approximate order of reaction with respect to substrate?

b The following mechanism has been proposed for enzyme-catalysed reactions (E = enzyme, S = substrate, P = product):

$$E + S \rightarrow ES \rightarrow EP \rightarrow E + P$$

Explain why your answer to **a** tells you that the first step in this mechanism is not the rate-determining step at high substrate concentration.

c At high substrate concentrations, all the enzyme active sites are occupied. This is known as active site *saturation*. Explain how this idea supports your answers to **a** and **b**.

d At lower substrate concentrations, there is a change in the way the rate depends on concentration. At very low substrate concentrations, the reaction is approximately first order with respect to the substrate. Suggest a reason for this.

Exercise 2

The results in Table 2 come from an experiment in which the concentration of urea (the substrate) was kept fixed and the concentration of urease (the enzyme) was varied. This was achieved by adding different volumes of urease solution to the reaction mixture, and keeping the total volume constant by making up with the appropriate volume of water.

Volume of urease solution/cm^3	Rate/mol dm^{-3} min^{-1}
0	0
0.050	0.6×10^{-6}
0.100	0.8×10^{-6}
0.200	1.8×10^{-6}
0.300	3.2×10^{-6}
0.500	4.8×10^{-6}
1.000	10.4×10^{-6}
1.500	14.9×10^{-6}
2.000	19.5×10^{-6}

Table 2

Plot a graph of the reaction rate against the volume of urease solution, which is a measure of the urease concentration (horizontal axis).

e What is the order of reaction with respect to the enzyme?

f Describe how your answer to **e** can be explained in terms of the mechanism proposed in **b**.

EP7

Check your notes on *Engineering Proteins*

This activity helps you get your notes in order at the end of this unit.

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.

- Proteins are condensation polymers formed from amino acid monomers.
- The general structure of amino acids.
- The acid–base properties of amino acids and the formation of zwitterions.
- The formation and hydrolysis of the peptide link between amino acid residues in proteins (**Storyline EP2**; **Activity EP2.2**).
- The use of paper chromatography to identify amino acids (**Activity EP2.2**).
- The importance of amino acid sequence in determining the properties of proteins, and the diversity of proteins in living things (**Storyline EP2**).
- Stereo-isomers: *cis-trans* and optical isomers (enantiomers).
- The use of the term *chiral* as applied to a molecule.
- How nuclear magnetic resonance (n.m.r.) spectroscopy can be used for the elucidation of molecular structure.
- The interpretation of n.m.r. spectra for simple compounds given relevant information (**Activity EP2.3**).
- The expression for the equilibrium constant, K_c, for a given reaction.
- The way in which changes of temperature and pressure affect the magnitude of the equilibrium constant.
- The use of values of K_c, together with given data on equilibrium concentrations, to calculate the composition of equilibrium mixtures.
- The primary, secondary and tertiary structures of proteins (**Storyline EP4**).
- The role of hydrogen bonds and other intermolecular forces in determining the structure and properties of proteins (**Storyline EP4**).
- The double helix structure of DNA in terms of a sugar–phosphate backbone and attached bases (**Storyline EP2**).
- The significance of hydrogen bonding in the pairing of bases in DNA, and the replication of genetic information (**Storyline EP2**; **Activities EP2.7** and **EP2.8**).
- How DNA encodes for the amino acid sequence in a protein.
- The use of empirical rate equations of the form: rate $= k[A]^m[B]^n$ where m and n are integers.
- The meaning of the terms: *rate of reaction*, *rate constant*, *order of reaction* (both overall and with respect to a given reagent).
- Experimental methods for measuring the rate of reactions.
- How to use experimental data to find the order of a reaction (zero, first or second order).
- How to use given data to calculate half-lives for a reaction.
- The industrial importance of enzymes (**Storyline EP6**).
- The characteristics of enzyme catalysis, including: specificity, temperature and pH sensitivity, and inhibition (**Storyline EP6**).
- The specificity of enzymes in terms of a simple 'lock and key' model of enzyme action.
- The technique of 'genetic engineering' and its applications (**Storyline EP3** and **EP5**).

SSI.1

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.

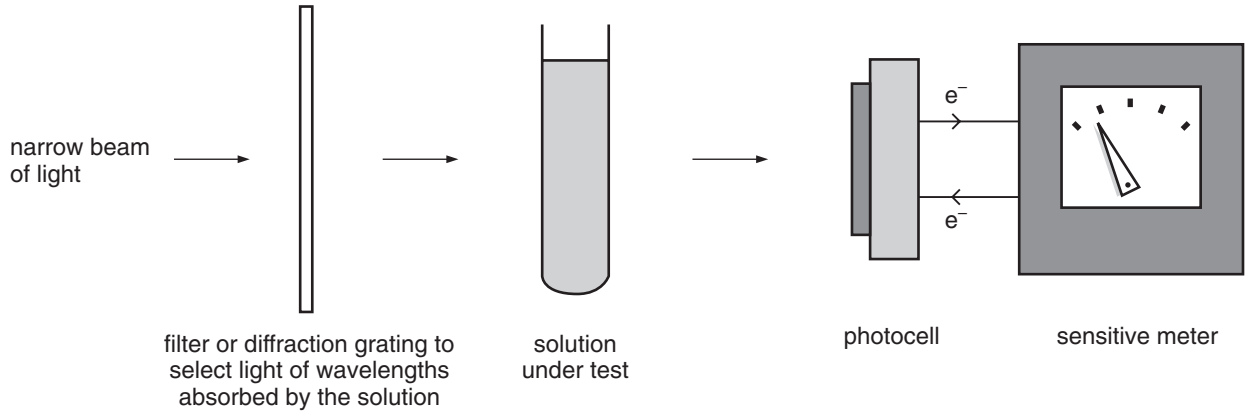


Figure 1 Simplified diagram of a colorimeter

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 cm^3 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?

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.)

SSI.2

A redox titration

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.

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.

SS2.1

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.

SS2.2

What changes occur during steelmaking?

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.

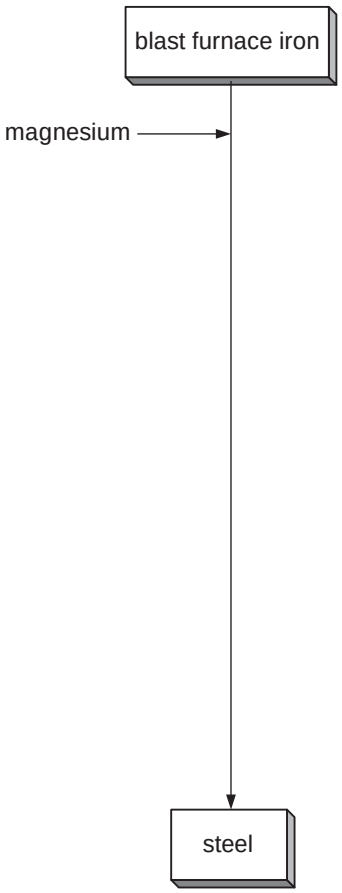


Figure 1 A flow diagram to show the production of steel from iron

SS2.3

Getting the 'heat balance' right (Optional extension)

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 x 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	16.8×10^3 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

SS2.4

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 = 1×10^6 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

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

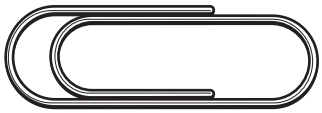
(High-carbon steels may well extend above 0.92% C in the coming years as new steels come on stream.)

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.



Aluminium

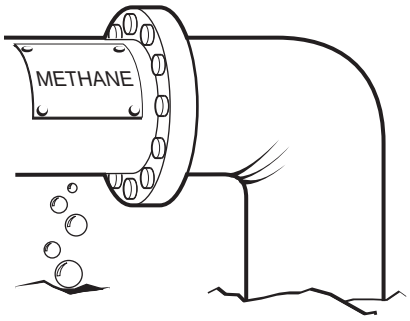
Aluminium is often added to the molten metal because it forms a fine precipitate of aluminium nitride as the steel solidifies; this limits the size of the crystals formed in the cooling metal. The resulting material can be easily shaped, yet is tough and has good impact resistance. Aluminium is added 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.

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).

Silicon

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

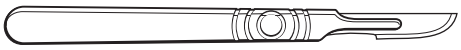


Vanadium

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).

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.



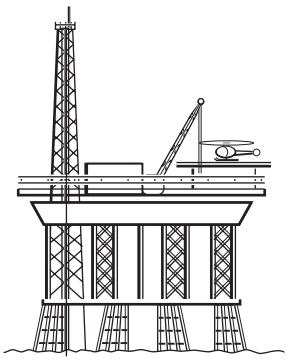
Niobium

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

Carbon

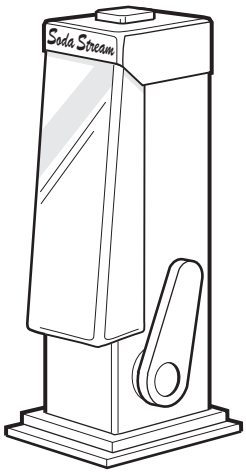
Carbon is the most important alloying element in steel. By changing the carbon content a wide variety of mechanical properties can be produced:

- 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.



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%.



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.

Tellurium

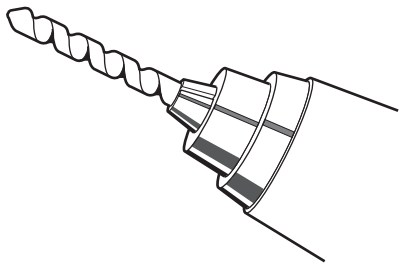
Tellurium is added to steels to improve machinability, either alone or with lead. Fumes from tellurium compounds can be noxious and proper venting must be provided whenever additions are made – otherwise workers can develop 'tellurium breath', with a strong garlic-like odour.

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.



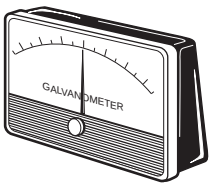
Manganese

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.

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.



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.

SS3.1

A simple redox reaction

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

zinc powder

CARE Eye protection must be worn.

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?

SS3.2

Simple electrochemical cells

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 cm^3 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 cm^3)
- iron(II) sulphate solution, 1.00 mol dm^{-3} (50 cm^3)
- zinc(II) sulphate solution, 1.00 mol dm^{-3} (50 cm^3)
- filter paper strips soaked in saturated potassium nitrate(V) solution
- high-resistance voltmeter (e.g. pH/mV meter)

copper(II) sulphate

CARE Eye protection must be worn.

Introduction

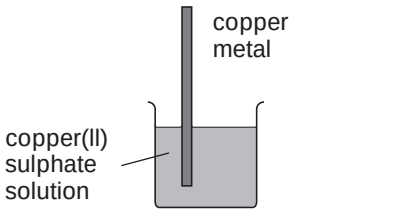
You have probably used batteries in a number of different appliances. They are often called 'dry' cells because, for convenience, pastes rather than solutions are used in making up the cells. They are all based on redox reactions arranged to occur in two half-cells. The electricity produced is generated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



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

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

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.

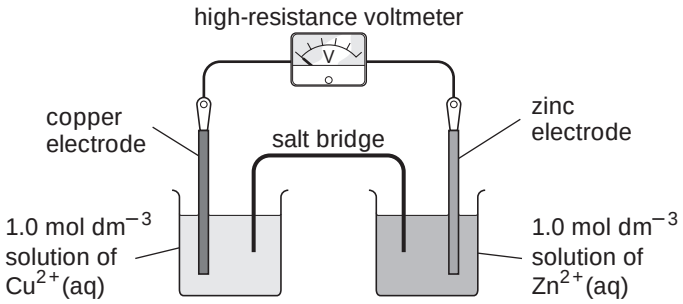


Figure 2 Arrangement for measuring the voltage of an electrochemical cell

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.

SS3.3

More electrochemical cells

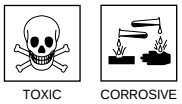
This activity extends your experience of half-cells to ones in which both reagents are in solution. You will investigate whether these half-cells can combine to make electrochemical cells in a way similar to metal ion/metal systems.* Chemical Ideas 9.2 *will help you interpret your results.

Requirements

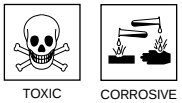
- copper(II) sulphate solution, 1.00 mol dm^{-3} (50 cm^3)
- copper metal strip (long enough to dip into the solution in the beaker)
- emery paper
- 100 cm^3 beakers (2)
- leads with crocodile clips (3)
- d.c. power supply able to give 3 V
- clean graphite electrodes (2)
- filter paper strips soaked 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



chlorine



copper(II) sulphate

CARE Eye protection must be worn.

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.

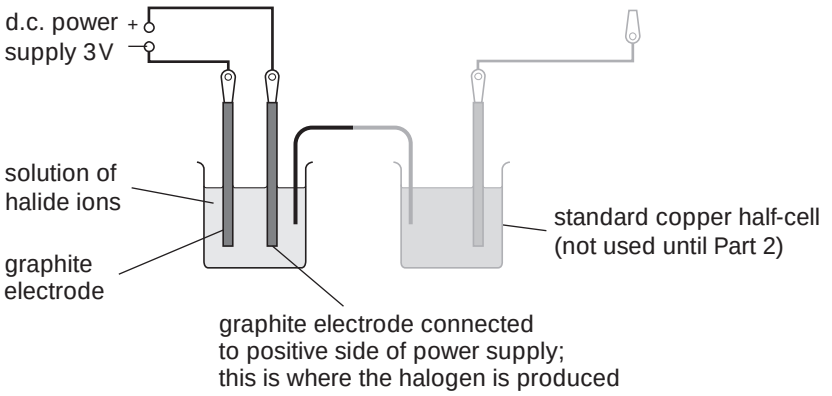


Figure 1 Arrangement for making the halogen/halide ion half-cell

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.

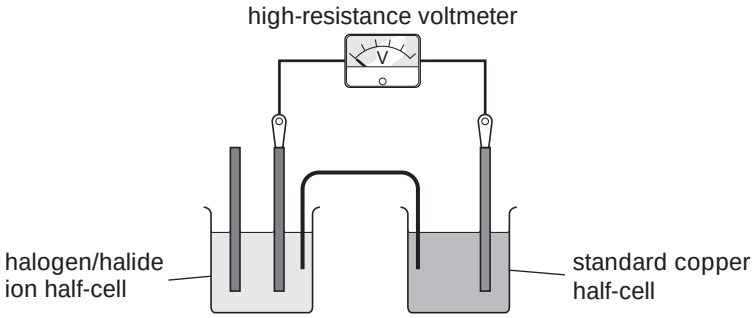


Figure 2 Arrangement for measuring the potential difference between a halogen/halide ion half-cell and a standard copper half-cell

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**.

SS3.4

How does steel rust?

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.)

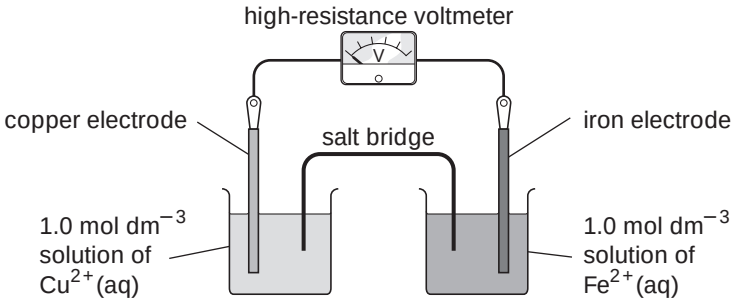


Figure 1 An electrochemical cell made up of Cu^{2+}(aq)/Cu(s) and Fe^{2+}(aq)/Fe(s) half-cells

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.

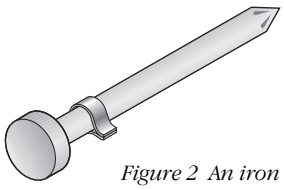


Figure 2 An iron nail in contact with copper

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.

SS3.5

Understanding redox reactions

***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.

SS5.1

Investigating the oxidation states of vanadium

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

CARE Vanadium compounds are toxic. Avoid skin contact.

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

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.**

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 cm^3 of 1.0 mol dm^{-3} sulphuric acid (**CARE** Irritant). Carefully add about 5 cm^3 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 cm^3 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 cm^3 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

SS5.2

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 cm^3 beaker
- 25 cm^3 measuring cylinder
- Bunsen burner, tripod and gauze
- 0–110 °C thermometer
- hydrogen peroxide solution, 20 vol (20 cm^3)
- 100 cm^3 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

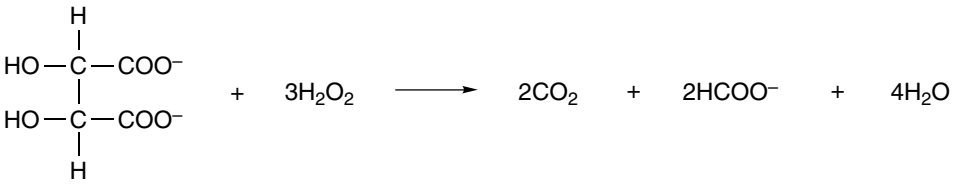
IRRITANT

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:



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 cm^3 of water in a 250 cm^3 beaker. Heat the solution to about 70 °C.

2 Heat 20 cm^3 of hydrogen peroxide solution (**CARE** Irritant) to approximately the same temperature in a 100 cm^3 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 cm^3 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 cm^3 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.

SS5.3

Looking at some transition metal complexes

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

dilute ammonia solution

copper(II) sulphate solution

concentrated hydrochloric acid

iron(III) chloride solution

nickel(II) chloride

sodium hydroxide solution

CARE Eye protection must be worn.

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?

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.

SS6

Check your notes on *The Steel Story*

This activity helps you get your notes in order at the end of this unit.

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 and subsequent reactions (**Storyline SS3**; **Activity SS3.4**).
- Approaches to corrosion prevention (**Storyline SS3**).
- Issues in the recycling of iron (**Storyline SS4**).