Salters Advanced Chemistry
Module 4 Activities Booklet

Chemistry by Design

2854

AA	Aspects of Agriculture
CD	Colour by Design
O	The Oceans
MD	Medicines by Design

Chemistry by Design

Module 4 – 2854 - Activities Booklet

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AA2.1

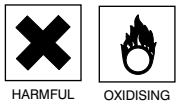
How does temperature affect the rate of a reaction?

In this activity you will develop a method for studying how an increase in temperature affects the rate of a reaction.

Requirements

- 0–110 °C thermometer
- boiling tubes
- test-tubes
- burettes (or 1 cm^3, 2 cm^3 and 5 cm^3 graduated pipettes)
- potassium iodide solution, 0.2 mol dm^{-3} (25 cm^3)
- potassium peroxodisulphate(VI) ($K_2S_2O_8$) solution, 0.01 mol dm^{-3} (35 cm^3)
- sodium thiosulphate ($Na_2S_2O_3$) solution, 0.01 mol dm^{-3} (20 cm^3)
- freshly made starch solution (10 cm^3)
- stopwatch
- 250 cm^3 beaker
- Bunsen burner, tripod and gauze

potassium peroxodisulphate(VI)



CARE Eye protection must be worn.

About the reaction

Peroxodisulphate(VI) ions oxidise iodide ions to form iodine:

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

In **Activity EP6.4** of **Engineering Proteins**, you used the 'iodine clock' method to investigate how the rate of this reaction varies with the concentration of one of the reactants. You measured the progress of the reaction by observing 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.

What you do

Use the 'iodine clock' technique from **Activity EP6.4**, and devise a procedure to investigate how the rate of the reaction varies in the temperature range 20 °C to 90 °C. It is important that the *concentrations* used throughout this experiment are kept constant: only the temperature is varied. Suitable volumes to use are:

- 3 cm^3 of 0.2 mol dm^{-3} KI(aq)
- 2 cm^3 of 0.01 mol dm^{-3} $Na_2S_2O_3$(aq)
- 1 cm^3 of starch solution
- 4 cm^3 of 0.01 mol dm^{-3} $K_2S_2O_8$(aq)

Collect your results in a table. Plot a graph of reaction rate against temperature, with temperature on the horizontal axis.

Describe the effect on the rate of the reaction of increasing the temperature. There is a rough rule that a rise of 10 °C in temperature causes the rate of many reactions to be approximately doubled. Is this true here?

You can read about the effect of temperature on the rate of a chemical reaction in **Chemical Ideas 10.2**.

QUESTION

How does increasing the temperature affect the rate constant (k) for the reaction?

AA3.1

What is the nitrogen content of soils? (Optional extension)

Activities AA2.5 *and* AA3.1 *form a pair of activities involving soils. You should aim to do at least* one *of them.*

This activity allows you to measure the amount in moles of nitrogen present in soil as ammonium ions and as nitrate(V) ions. You will be able to practise the techniques of steam distillation and titration.

Requirements

- oven-dry soil (30 g)
- 250 cm^3 stoppered bottle
- potassium chloride solution, 2.0 mol dm^{-3} (200 cm^3)
- filter funnel
- filter paper
- 250 cm^3 conical flasks (2) and bung
- apparatus for steam distillation (Figure 1)
- 50 cm^3 measuring cylinder
- magnesium oxide (0.5 g)
- boric acid, 1% solution (5 cm^3)
- Devarda's alloy (0.5 g)
- burette and titration apparatus
- sulphuric acid, 0.00500 mol dm^{-3} (50 cm^3)
- 100 cm^3 volumetric flask
- 10 cm^3 pipette
- 25 cm^3 pipette
- safety filler
- indicator solution (pH range 5–6), 1:1 mixture of Methyl Red and Bromocresol Green (100 mg in 100 cm^3 of ethanol)

indicator solution

HIGHLY FLAMMABLE

CARE Eye protection must be worn.

WEAR EYE PROTECTION

Introduction

Nitrogen available to plants exists in soil in two forms: as ammonium ions, and as nitrate(V) ions. The method you will use to determine the nitrogen content of your soil sample is a method still used for accurate determinations. The quicker, more convenient methods are less sensitive.

Work in groups for this activity. Half the students in each group can determine the nitrogen present as ammonium ions, in Part 2. The other half can determine the total nitrogen present as nitrate(V) and ammonium ions, in Part 3. You can then combine your results to work out the nitrogen present as nitrate(V) ions. Part 1 can be done in advance and the filtrate stored in a stoppered flask in the fridge until required. There will be enough solution for both halves of the group.

Ammonium ions are displaced into solution by ion exchange when the soil is shaken with a solution containing excess potassium ions. If the solution is then made alkaline, ammonia is formed, and can be distilled off. A **steam distillation** technique is used (see below) to make sure that ammonia remains in solution and does not escape as a gas.

The ammonia produced is absorbed in a 1% solution of boric acid:

$$NH_3(aq) + H_3BO_3(aq) \rightleftharpoons NH_4^+(aq) + H_2BO_3^-(aq)$$

The borate formed can then be titrated with a strong acid, like sulphuric acid:

$$H_2BO_3^-(aq) + H^+(aq) \rightarrow H_3BO_3(aq)$$

A mixed indicator solution containing Methyl Red and Bromocresol Green gives a sharp end-point from blue-green to pink.

The amount in moles of ammonia is equal to the amount of $H^+(aq)$ used in the titration. This titration procedure is used to reduce the risk of loss of ammonia.

Nitrate(V) ions are also present in the soil solution at the end of Part 1. These are converted to ammonium ions by a reducing agent. Distillation as before, followed by titration, gives the *total* available nitrogen in the soil. The amount present as nitrate(V) can then be found by subtraction.

What you do

Part 1: Extraction of ammonium ions

1 Put 200 cm^3 of 2.0 mol dm^{-3} potassium chloride solution into a bottle. Add 30 g of dry soil. Stopper the bottle and shake it for 10 minutes.

2 Filter the mixture into a conical flask. Stopper the flask and store it in a fridge until required.

QUESTIONS

a Write an equation to represent what is happening as the soil is shaken with the potassium chloride solution.

b Why is such a large volume of 2.0 mol dm^{-3} potassium chloride solution used?

Part 2: Determination of nitrogen present as ammonium ions, NH_4^+

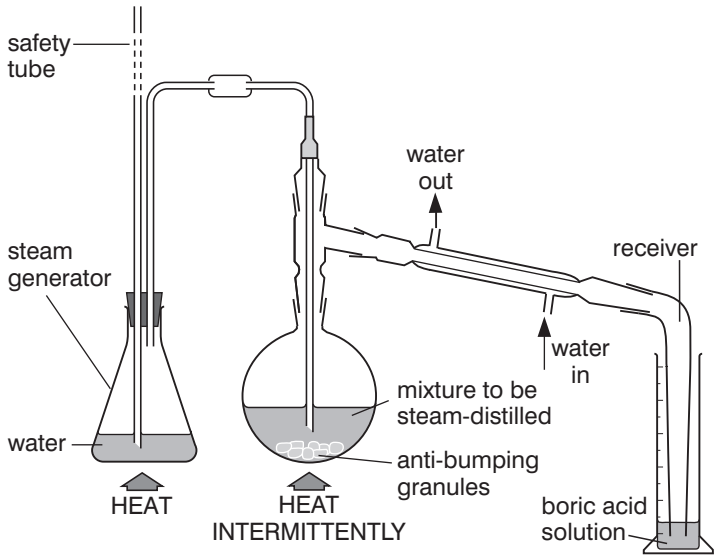


Figure 1 Apparatus for steam distillation

3 Set up the apparatus for steam distillation, as shown in Figure 1.

4 Place 50 cm^3 of the filtrate from Part 1 into the round-bottomed flask and add 0.5 g of magnesium oxide. (The MgO reacts with the NH_4^+ ions, liberating ammonia.) Put 5 cm^3 of boric acid in the measuring cylinder you are using to collect the ammonia solution.

5 Heat the water in the steam generator. When it boils, steam passes through the mixture in the round-bottomed flask. This flask should be heated gently to prevent steam condensing.

Steam distil until about 40 cm^3 of distillate have been collected. The distillate should contain all the ammonia released from your soil sample.

The distillation will take some time. While it is being carried out, one of you should set up a burette filled with 0.00500 mol dm^{-3} sulphuric acid ready for the titration.

6 At the end of the heating be careful to avoid any 'sucking back'. Before turning off the heat, lower the receiver and rinse it with a little distilled water into the measuring cylinder, and then disconnect the steam generator.

7 Transfer the distillate to a 100 cm^3 volumetric flask and make up to the mark with distilled water. Stopper the flask and shake it well. Using a pipette fitted with a safety filler, transfer 10 cm^3 of the solution to a 250 cm^3 conical flask. Add 2 or 3 drops of indicator solution and do a rough titration to get used to the end-point. This will also allow you to decide on the most suitable volume of solution to remove for the accurate titration. Make a note of this volume.

8 Now carry out an accurate titration and record the volume of sulphuric acid you used.

Part 3: Determination of nitrogen present as nitrate(V) ions, NO_3^-

9 Set up the apparatus for steam distillation as shown in Figure 1. Put 5 cm^3 of boric acid in the measuring cylinder you are using to collect the ammonia solution.

10 Devarda's alloy contains copper and aluminium and acts as a reducing agent. It reduces nitrate(V) ions to ammonia in alkaline solution. Place 50 cm^3 of the filtrate from Part 1 into the round-bottomed flask, and add 0.5 g of Devarda's alloy and 0.5 g of magnesium oxide. (The MgO reacts with the NH_4^+ ions, liberating ammonia.) Steam distil the mixture as described in steps **5** and **6** until you have collected 40 cm^3 of distillate. During the distillation, one of you should set up a burette filled with 0.00500 mol dm^{-3} sulphuric acid ready for the titration.

11 Transfer the distillate to a 100 cm^3 volumetric flask and make up to the mark with distilled water. Stopper the flask and shake it well. Using a pipette fitted with a safety filler, transfer 10 cm^3 of the solution to a 250 cm^3 conical flask. Add 2 or 3 drops of indicator solution and do a rough titration to get used to the end-point. This will also allow you to decide on the most suitable volume of solution to remove for the accurate titration. Make a note of this volume.

12 Now carry out an accurate titration and record the volume of sulphuric acid you used.

QUESTIONS

c Write an equation for the reaction between ammonium ions and magnesium oxide in steps **4** and **10**.

d Write an equation for the reaction of the distillate solution with sulphuric acid.

Working out your results

13 Use the titration results in step **8** to calculate the amount in moles of ammonia produced from your soil sample in Part 2. This is the amount of nitrogen in the soil in the form of NH_4^+ ions.

14 Use the titration results in step **12** to calculate the amount in moles of ammonia produced from your soil sample in Part 3. This represents the *total* amount of nitrogen in the soil in forms usable by plants (NH_4^+ and NO_3^-).

15 Work out the amount in moles of NO_3^- ions present in the soil sample.

16 Use the values obtained in steps **13–15** to calculate the *mass* of nitrogen present in the soil sample as:
- **a** ammonium ions
- **b** total usable nitrogen
- **c** nitrate(V) ions.

17 1 hectare of soil to a depth of 20 cm has a mass of about 2500 tonnes. Use your answer to step **16b** to calculate the total mass of nitrogen, in forms usable by plants, in the top 20 cm layer of 1 hectare of your soil.

AA3.2

The nitrogen balance in UK agriculture

The purpose of this activity is to allow you to become more familiar with the nitrogen cycle and to help you appreciate the quantities of nitrogen involved.

What you do

Figure 1 shows a modified version of the diagram of the nitrogen cycle from **Storyline AA3**. The reserves of nitrogen in the soil and in the atmosphere are shown, but the ovals showing the nitrogen fluxes have been left blank.

1 Using data from Table 1, enter values for the total annual fluxes of nitrogen in UK agricultural land into the appropriate spaces in the diagram. You may like to use different coloured pens for the input and output figures.

Input	Thousands of tonnes per year	Output	Thousands of tonnes per year
Rain	275	Crops and grasses (mostly for animal feed)	1367
Seeds	14	Leaching	326
Fertilisers	1150	Loss of ammonia as gas	
Sewage	26	from livestock excreta	536
Livestock excreta	1020	from crop wastes	50
Silage effluent	9	from sewage	9
Crop waste	24	Denitrification and immobilisation	380
Biological N_2 fixation	150		

Table 1 Nitrogen balance in UK agriculture. The figures (produced by the Royal Society in 1983), are estimated totals for the UK in thousands of tonnes of nitrogen per year, showing the inputs and outputs of nitrogen in agricultural land.

These estimates, although originating in the 1970s, still remain the best available data. It is accepted that the proportions between the various inputs and between the outputs are similar to those obtained now.

2 Refer to the section on the nitrogen cycle in **Storyline AA3**. Mark on Figure 1 the formulae for the different forms of inorganic nitrogen in the cycle to show the conversion from one form to another.

QUESTIONS

a Work out the *total input* of nitrogen into agricultural land in the UK in thousands of tonnes per year. Now work out the *total output* of nitrogen. Comment on the relative sizes of the two figures. Compare the size of these fluxes with the size of the *total reserves* of nitrogen for the UK.

b Make a list of the inorganic ions and molecules involved in the nitrogen cycle. Identify the oxidation state of nitrogen in each species.

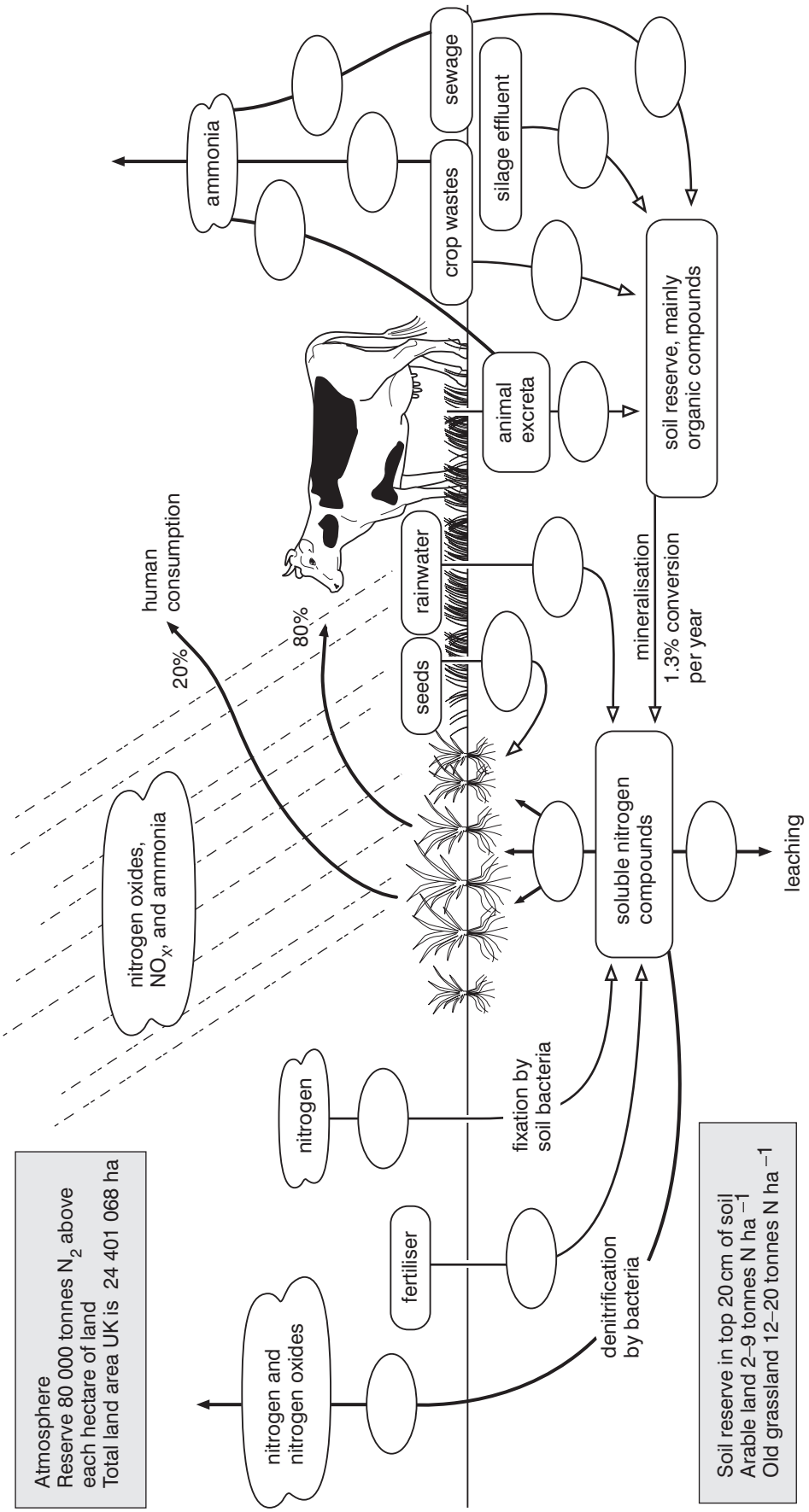


Figure 1 The nitrogen balance in UK agriculture (Source of figures: Royal Society 1983; MAFF 1984). Numbers to be inserted are totals for the UK in thousands of tonnes N per year

AA3.3

Revising for end of course exams

As you approach the end of the course you will need to revise most of the work you have covered. The aim of this activity is to help you do this effectively.

You may wish to delay doing this activity until the most appropriate time for you* – but don't leave it too late. *You need plenty of time to plan your revision programme well.

Synoptic assessment

An important part of the end of course examinations involves **synoptic assessment**. This requires you to draw together knowledge, understanding and skills learned in different parts of the course. You should feel confident about this, as many of the storylines you have studied have required you to use ideas from different areas of chemistry. Real-life contexts can rarely be fully understood through a knowledge of a single area of chemistry. However, in your revision and in thinking about how you will approach examination questions you have to acknowledge that the questions are designed to test your ability to:

- recognise the different chemical ideas you need to use to answer the question
- draw on your knowledge and understanding of these ideas to construct your answer.

The synoptic examination is based on the units at the end of the course, but remember that these units bring together many ideas that you have met in earlier units.

Some questions will be based on applications you have not met during the course. Hopefully these will be interesting contexts and you may even enjoy applying your chemical understanding to tackling the problems you are set.

Be active

A long time ago, in **Activity DF4.8**, you were encouraged to be as active as possible while revising. You should now have developed your own revision strategies, based on a variety of tasks that you set yourself, but it may still be worthwhile looking back at the few suggestions given in that activity.

Drawing up an action plan

A revision action plan will ensure that you cover the aspects of the course that you need and will minimise the temptation to drift randomly from one topic to another.

First of all, make a list of the weeks available for work before the exam. Divide the work you need to do between these weeks, making sure that all the units in the course are covered. Do not assign work to the day or two before the exam – you will need this time for checking on small points, not major revising.

Now, write out a diary of all the times you have available to revise chemistry during the next week. Divide this time up into hour-size chunks (or whatever size suits you best), with breaks in between.

Next, allocate a different topic to each chunk of time. It is a good idea to cover something from each unit in the course during the week.

Finally, *stick to your plan*. When you have reached the end of the week make up a new diary in a similar way to build on the revision you have already completed.

Using your resources

Using the summary activities

The summary activity at the end of each unit tells you what you need to know from that unit and should have helped you to acquire an 'overview' of the unit. Most of the information will be covered in the **Chemical Ideas**, but if the *main* source of information is the **Storyline** or an **Activity**, this will be indicated. Don't forget to look at the Activities. You should be able to describe and draw diagrams for basic techniques, such as heating under reflux or carrying out a distillation.

If you have made good notes under the summary headings for each unit you will have produced your own invaluable resource. Now is the time to make good use of it.

Using the Chemical Ideas *book*

The **Chemical Ideas** book is a good revision aid. The concepts are arranged in chemical themes. By reading a whole chapter you can get an 'overview' and see how the various parts from different units fit together.

Using problems and assignments

For the topic which you are revising, pick out relevant problems from the chemical ideas sections and assignments from the stories. Write down your answers on a blank sheet of paper before comparing them with your answers from earlier in the course. You will find that this approach works particularly well for mathematical calculations.

Using past exam papers

Attempting past exam papers is helpful in a number of ways. They will provide a 'yardstick' against which you can measure how well your revision is going. You will become aware of the detail in which you need to know a topic and also get a flavour of the way in which questions are worded.

Try to identify the unit and summary headings to which each part of a question relates. This will help you to understand what is required when you meet new questions.

Working with another chemistry student

This can often provide an effective and stimulating change from working on your own. Question each other about the facts and also about the main ideas in the course. You need to ask *why?* and *how?* questions, as well as *what?*, *which?* and *where?* questions. Your exam will test you not only on your knowledge of the facts but also on your understanding and your ability to make comparisons and be critical.

And finally …

Finally, a few words of encouragement. Almost everyone finds written exams stressful and daunting. However, students who revise thoroughly and work to a planned programme are likely to put themselves under less pressure and achieve their best result on the day.

AA4.I

Dilemma over malaria

This activity provides an opportunity for you to consider the role of chemistry in fighting disease, in monitoring the environmental impact of pesticides and in decision making.

The short article reproduced on the next sheet was written by Bette Hileman and appeared in *Chemical and Engineering News*, published by the American Chemical Society, in September 1999. It outlines succinctly the dilemma facing those who are responsible for decisions about the use of DDT and those who determine the focus of future research. The global perspective in the article highlights the likelihood that different societies will have different views on the issue and that there are worldwide as well as local environmental concerns.

The intention is that you should prepare for a group discussion on the *Dilemma over malaria* and that the discussion should aim to reach agreement on what you as a group of chemistry students think would be appropriate short-term and long-term policies for dealing with malaria throughout the world.

What you do

1 Read through the article and make a note of the factors that are important in deciding appropriate policies for dealing with malaria.

2 Decide which of these factors can be supported by scientific evidence and search for additional articles and data that are relevant to the environmental concerns and the health concerns.

One way of doing this is to search the Internet for sites concerned on the one hand with *DDT* and on the other with *malaria*. It would be more efficient if some members of the group concentrated on information about malaria, its effects and its treatment, whereas others could concentrate on the environmental concerns. When extracting information from other sources try to distinguish between evidence and opinions.

3 Prepare brief presentations which you think should be considered as the group formulates its policy proposals.

government insights

Dilemma over malaria

Earlier this month, about 110 nations met in Geneva under the auspices of the United Nations Environment Program to negotiate the phaseout of 12 persistent organic pollutants (POPs). One of the most contentious issues they faced was whether to ban all uses of the pesticide DDT or to allow its continued use to kill malaria-transmitting mosquitoes until equally inexpensive alternatives have been developed.

Many industrialized countries and the World Wildlife Fund (WWF) pressed for a strict ban on all uses of DDT by 2007. Some public health groups and a number of developing countries pleaded for continued DDT use to fight malaria.

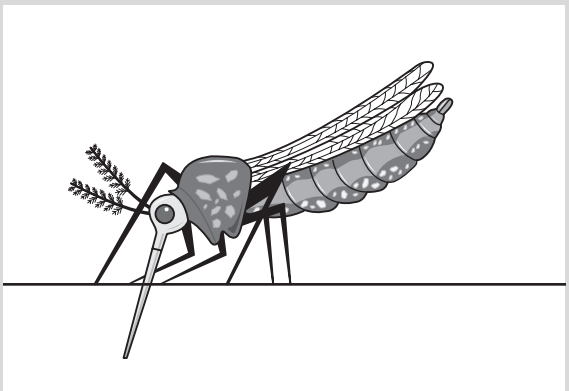
As a journalist who cares very much about both the environment and public health, and as the mother of a daughter who lives in Nairobi and has contracted malaria, I have encountered few questions that pose a more difficult dilemma. On the one hand, I know many reasons why DDT should be banned worldwide. DDT brought a number of bird species to the brink of extinction, and now that global use has declined, those species are recovering. DDT is so persistent that 10 to 35 years after it is applied to a field, half of it remains in the soil.

Because DDT is transported to the Arctic on ocean currents and through the atmosphere on soil particles, the levels of DDT in Arctic mammals at the top of the food chain is very high. However, on a global scale, the situation is improving. The average level of the pesticide in human fat has declined from 12 ppm in the early 1970s to less than 7 ppm today.

In South Africa, where DDT was heavily used in agriculture, breast-fed children receive five to 18 times as much DDT from milk as the World Health Organization recommends as an acceptable daily intake. Some studies show that DDT shortens the time of lactation.

In addition, DDT and its metabolites may have more subtle effects on human health. Animal studies indicate that DDT and its metabolites cause male birth defects and compromise the immune system.

On the other hand, there are many compelling reasons why DDT for malaria control should not be banned by 2007. It is still the cheapest and, in some places, the most effective way to control mosquitoes. The one Latin American country where malaria incidence has declined, Ecuador, is the only one that has increased its use of DDT to kill mosquitoes. Malaria, a serious infection of *Plasmodium* parasites, is one of the resurgent diseases in the world today. Each year, it causes 500 million clinical cases and kills up to 2.7 million people, many of whom are children under five. The incidence of malaria is increasing, partly because insect spraying programs have been cut back, partly because prevention programs using antimalarials have been abandoned, and partly because of global climate change. As temperatures increase at higher elevations, malaria-carrying mosquitoes extend their range, infecting people who have no natural immunity.



The inexpensive drug chloroquinine that people around the world used for years to prevent and control the disease is no longer effective because the malaria parasites have developed resistance to it. Since the alternative drugs are much more expensive, most cases of malaria go untreated.

If the inside walls of a house are painted with DDT, mosquitoes are controlled for six months to a year. Some mosquitoes are resistant to DDT, but these tend to be irritated by it, so they leave the house after coming in contact with the walls. Painting the inside walls of a large house requires 400 g to 600 g of DDT. After six months, about half the original application usually flakes off the walls and most of this ends up outdoors. But this amount is minuscule compared with the 800 kg used on a 100-acre cotton field in a growing season.

WWF argues that malaria-carrying mosquitoes can be controlled by altering the environment. It advocates planting trees to dry up the soil, stocking ponds with mosquito-larvae-eating fish, and emptying water from containers so mosquitoes cannot breed. In some dry areas–where malaria transmission rates are moderate–such remedies may work.

However, mosquitoes in some locales breed almost anywhere, in grass and wet leaves, in any small depression in a farm plot, in rain gutters and drainage ditches, in plants that hold small amounts of water. The eggs persist through droughts, waiting for the next rain or monsoon. Then, hordes of mosquitoes burst forth and often land on humans at a rate up to 100 a minute.

WWF also advocates the use of bed nets soaked in pyrethroid insecticides and the limited spraying of pyrethroids inside houses to kill mosquitoes. Pyrethroids are much less persistent than DDT. However, millions of people cannot afford bed nets, and spraying pyrethroids by most accounts is about three times as expensive as painting interior walls with DDT.

DDT is still used on crops in much of Africa, India, and perhaps China. To me, it seems that the best compromise for the POPs treaty would be a strict ban on agricultural uses of DDT and a total phaseout for public health use when cheap, effective alternatives are available.

This might put pressure on industrialized countries to put money into research on malaria drugs and vaccines and on mosquito control. Just $84 million is spent worldwide annually on malaria research. Even the world's best malaria drug research lab, the Walter Reed Army Institute of Research, Washington, D.C., now receives only $5 million a year for malaria drug research. No major pharmaceutical company is working on a malaria drug.

If we as a society want a total ban on DDT, our government should be willing to invest a large part of the money it will take to reduce the disease burden from malaria. As travellers and as temporary inhabitants in endemic areas, we would also benefit.

Bette Hileman

AA4.2

Partition equilibrium

In this activity you will investigate the way in which a solid behaves when it can dissolve in two solvents which do not mix. Next you will plan a procedure for making quantitative measurements. You can then use data on some pesticides to look at the link between values of partition coefficients and the concentrations of pesticides in living organisms.

Requirements

- iodine crystals (2 small crystals)
- forceps
- rack and test-tubes with rubber bungs
- dropper pipettes
- cyclohexane (4 cm^3)
- potassium iodide solution, 0.2 mol dm^{-3} (10 cm^3)

CARE Iodine is harmful. Use forceps to pick up the iodine crystals. When you have finished, place the iodine solutions in the 'iodine residues' container.

CARE Cyclohexane is highly flammable.

cyclohexane

HIGHLY FLAMMABLE

iodine

HARMFUL

CARE Eye protection must be worn.

WEAR EYE PROTECTION

Part 1: The partition of iodine between two solvents (May be a teacher demonstration)

A substance may be soluble in two solvents which do not mix, like water and cyclohexane. In this part of the activity you will investigate the way iodine partitions between these two solvents. Iodine is only sparingly soluble in water, but it dissolves readily in potassium iodide solution. In these experiments, therefore, potassium iodide solution is used instead of pure water. (When iodine dissolves in potassium iodide solution, it forms the brown complex ion, I_3^-(aq). This is why iodine is so much more soluble in this solvent than it is in water.)

Solutions of iodine in cyclohexane and aqueous potassium iodide are coloured, so you can draw qualitative conclusions about the concentration of iodine in each layer from the appearance of the two layers.

What you do

1 Take two *small* iodine crystals (**CARE** Harmful. Use forceps to pick up the crystals) of approximately the same size, and place each crystal in a test-tube. Add 2 cm^3 of cyclohexane (**CARE** Highly flammable) to one tube and 2 cm^3 of aqueous potassium iodide to the other. Stopper the tubes and shake gently until the iodine crystals dissolve. Note the colour of each solution.

2 Now add 2 cm^3 of aqueous potassium iodide to the tube containing iodine dissolved in cyclohexane, and 2 cm^3 of cyclohexane to the tube containing iodine dissolved in aqueous potassium iodide. Stopper the tubes, shake them for a few minutes and stand them in a rack to allow the layers to separate.

3 Using a pipette, draw off the upper, cyclohexane layer from one of the test-tubes and place this solution in a clean test-tube. Investigate the effect of adding further volumes of the second solvent to each of the separated layers.

4 Record your observations, noting the colour and intensity of colour in each layer. What do your observations tell you about the way iodine partitions itself between the two solvents?

You will have found that some of the iodine dissolves in one solvent, and some in the other. The partition of iodine between the two solvents is an equilibrium process. The ratio

$$\frac{\text{concentration of solute in solvent A}}{\text{concentration of solute in solvent B}}$$

is a constant at a given temperature, and is called the **partition coefficient**. It is an equilibrium constant. You can read more about it in **Chemical Ideas 7.4**.

Part 2: Partition coefficients and pesticides

Pesticide activity is often linked to the ability of pesticide molecules to move rapidly out of aqueous solution into fatty tissues in cell membranes. To achieve this they must be much more soluble in non-polar solvents than in water. Octan-1-ol is a relatively non-polar solvent, and the partition coefficient K_{ow} is frequently quoted for pesticides:

$$K_{ow} = \frac{\text{concentration of compound in octan-1-ol}}{\text{concentration of compound in water}}$$

The fate of pesticides in the environment is important. They can accumulate in living organisms, then become more and more concentrated up the food chain.

Measurements of this **bioconcentration** have been made in fish. For any compound, the **bioconcentration factor** is equal to

$$\frac{\text{concentration of compound in whole fish}}{\text{concentration of compound in water}}$$

The bioconcentration factor does not depend much on the species of fish, or on the length of time the fish has been in pesticide-contaminated water (once the system has come to equilibrium): it is a property of the pesticide itself. Determining the bioconcentration factor is an important but expensive business. Researchers have therefore looked for ways of estimating bioconcentration factors from properties which are easier to measure, such as partition coefficients, particularly K_{ow}.

Table 1 shows lg K_{ow} and lg(bioconcentration factor) for several pesticides.

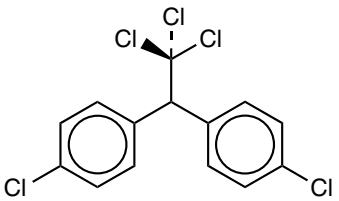
Pesticide	lg K_{ow}	lg(bioconcentration factor)
Organochlorines		
chlordane	6.00	4.58
DDT	5.98	4.47
DDE	5.69	4.71
DDD	6.02	4.81
dieldrin	5.16	4.10
lindane	3.85	2.51
Pyrethroids		
permethrin	5.00	3.70
Hydrolysis products of permethrin		
alcohol	2.94	1.35
acid	2.00	0.74
Others		
atrazine	2.63	0.48
dibenzofuran	4.12	3.13

Table 1 Data on bioconcentration factors for some pesticides and some of their breakdown products. Note that in both columns logarithmic values are quoted.

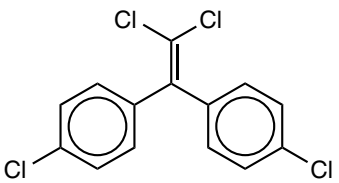
QUESTIONS

a Plot a graph of lg(bioconcentration factor) against lg K_{ow}. What is the relationship between the two quantities?

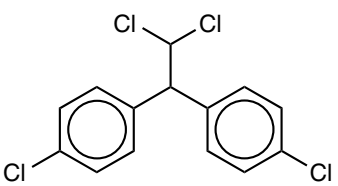
b The ester group in permethrin is rapidly hydrolysed in the environment (see **Storyline AA4**, 'The pyrethroid story'). DDT is degraded to DDE and DDD.



DDT



DDE



DDD

Refer to the values of lg K_{ow} in Table 1. Suggest why DDT and its breakdown products DDE and DDD may persist for years, causing problems in the environment, whereas permethrin does not cause similar problems.

AA4.3

What makes an active pyrethroid?

In this activity you will identify features which are important for insecticidal activity in pyrethroids. This will help you to pick out common structural features in complex organic molecules.

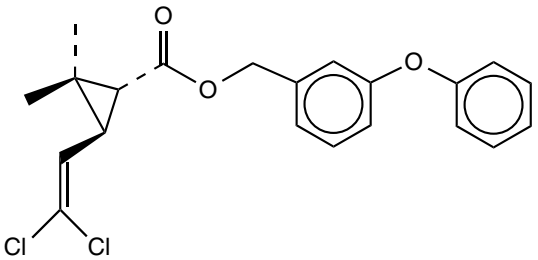
Introduction

Pyrethroids kill insects by binding to specific proteins in nerve-cell membranes. As a result the nervous system cannot function properly and the insect dies. In order for them to work, pyrethroids must have the correct physical properties so that they can move into the cell membranes. They need to have groups of the right kind in the right positions so that intermolecular forces can bind the pyrethroid molecules to proteins in the nerve cell membranes. Finally they should be easily hydrolysed so that they do not persist in the environment.

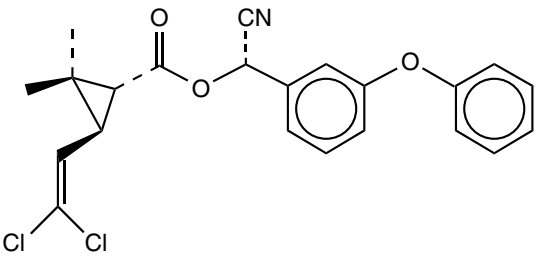
What you do

Work in groups so that you can discuss your ideas.

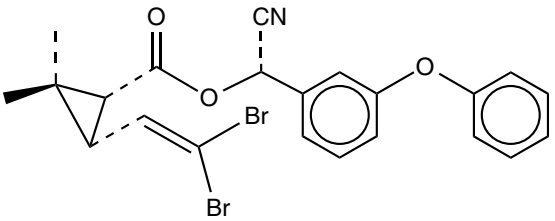
1 Identify structural features which are common to the pyrethroid molecules mentioned in **Storyline AA4**, 'The pyrethroid story'. These are the compounds A, B and C shown below. One way to do this is to list the structural features present in biopermethrin in a table, and tick off features which are also present in B and C.



A *Biopermethrin*

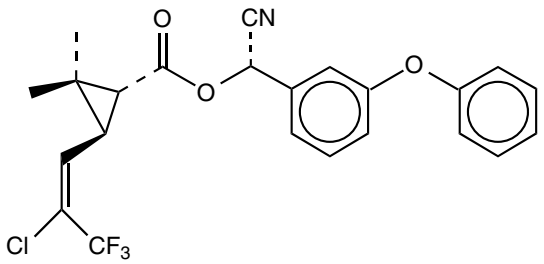


B *Biocypermethrin*

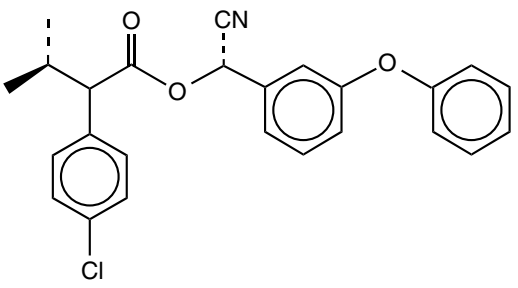


C *Deltamethrin*

2 Identify three features of A, B and C which are still present in D and E. Compare the structures of D and E with biocypermethrin, structure B. Where there has been a change, what replaces the group or groups removed?

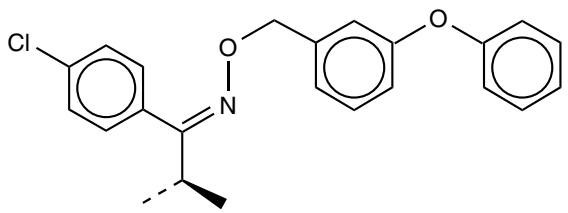


D

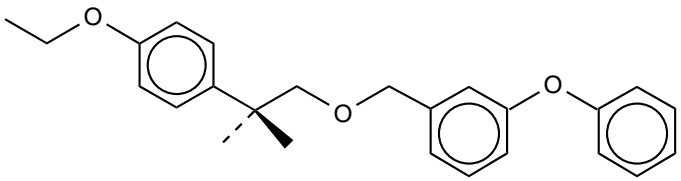


E *Fenvalerate*

3 Now inspect F and G, which are also insecticides:



F



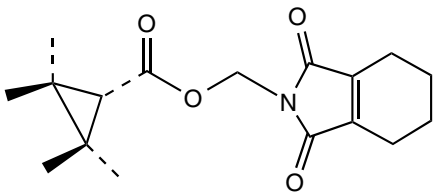
G

Are any of the features which you identified in A, B and C still present? Do the structures have anything in common with fenvalerate, E? If you cannot see any, check with your teacher rather than spend a long time searching.

You may be surprised by how few of the groups present in permethrin are *essential* for insecticidal activity. It appears that active pyrethroids have unsaturated groups at each end of the molecule (alkene or benzene) and that pairs of methyl groups are present. The distance between the methyl groups and the unsaturated end groups is important for activity.

Overall, the compounds must be non-polar, with high K_{ow} values (see **Activity AA4.2**). The presence in the centre of the molecule of a group which is easily hydrolysed means that the compounds are not persistent in soil.

4 Inspect structure H below. The substance is a rapid knock-down agent but does not kill insects. They recover from its effects. What features are missing which were present in all the other pyrethroid molecules?



H

Does this confirm or conflict with the suggestion in **3** above about features identified as important for insecticidal activity of pyrethroids?

AA5

Check your notes on *Aspects of Agriculture*

This activity helps you to 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.

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 ways in which chemists can help improve food production, including providing extra nutrients, controlling soil pH and controlling pests (the **Storyline** in general).
- The effect of temperature on the rate constant of a reaction.
- The interpretation of silicate structures in terms of the tetrahedral silicate unit (**Storyline AA2**; **Activity AA2.2**).
- The interpretation of the propreties of clay minerals in terms of a simple model of layers made up of tetrahedral silicate sheets and octahedral aluminate sheets (**Storyline AA2**; **Activities AA2.2** and **AA2.3**).
- The role of ion exchange processes in soil and the ion-exchange characteristics of different soils (**Storyline AA2**).
- The principles of ion exchange.
- The relationship of ion exchange behaviour of anions and cations to ionic size.
- The effect of atomic number, charge and hydration on the size of anions and cations.
- The relationship between ionic size and properties.
- The redox reactions involved in the interconversion of the following species in the nitrogen cycle: nitrogen gas, nitrate(V) ion, nitrate(III) ion, ammonium ion, dinitrogen oxide (N_2O), nitrogen monoxide (NO), nitrogen dioxide (NO_2) (**Storyline AA3**; **Activity AA3.2**).
- An outline of the manufacture of ammonia by the Haber Process, including essential conditions (**Storyline AA3**).
- Why the conditions in the Haber Process are chosen, including the effect the conditions have on the position of equilibrium and on the rate of reaction (**Storyline AA3**).
- The expression for the equilibrium constant, K_p, for reactions involving gases (in terms of partial pressures).
- How values of K_p, together with given data on partial pressures, are used to carry out calculations concerning the composition of equilibrium mixtures.
- The trends in reactions of the elements, and the properties of their compounds, across a period in terms of structure and bonding, including: the reactions of the elements with oxygen, chlorine and water; the acid–base character of oxides; the behaviour of chlorides towards water.
- The relationship between the structure and bonding of a substance and its properties.
- The partition equilibrium that occurs when a solute is distributed between two immiscible solvents.
- The design of pesticides that combine maximum efficacy with minimum environmental damage (**Storyline AA4**).

CDI

Changing colours chemically

In this activity you will investigate colour changes brought about in a variety of ways, and then identify the type of reaction involved in each case.

Requirements

- 250 cm^3 stoppered bottle
- 100 cm^3 measuring cylinder
- alkaline solution of glucose (100 cm^3)*
- Methylene Blue indicator
- Phenolphthalein and Fluorescein indicators (optional)
- boiling tubes, test-tubes and rack
- acidified solution of ammonium vanadate(V) (ammonium metavanadate, NH_4VO_3) (10 cm^3)*
- zinc (granulated)
- zinc oxide (0.5 g)
- Bunsen burner
- lead nitrate(V) (ground to a powder) (0.5 g)
- potassium iodide (ground to a powder) (0.5 g)
- lead nitrate(V) solution, 0.5 mol dm^{-3} (3 cm^3)
- potassium iodide solution, 0.5 mol dm^{-3} (1 cm^3)
- teat pipettes
- sodium carbonate solution, 1.0 mol dm^{-3} (1 cm^3)
- dilute ammonia solution, 2.0 mol dm^{-3} (5 cm^3)
- potassium (or ammonium) thiocyanate solution, KSCN (or NH_4SCN), 0.1 mol dm^{-3} (1 cm^3)
- potassium hexacyanoferrate(II) solution, $K_4Fe(CN)_6$, 0.005 mol dm^{-3} (1 cm^3)
- dilute solutions (approximately 0.1 mol dm^{-3}) containing the following ions (1–2 cm^3 of each solution):
  – copper(II)
  – nickel(II)
  – iron(III)
- potassium chromate(VI) solution, 0.5 mol dm^{-3} (2 cm^3)
- protective gloves
- dilute sulphuric acid, 1.0 mol dm^{-3} (1 cm^3)
- microscope
- slides and coverslips
- rubber bungs
- Universal Indicator solution
- sodium hydroxide solution, 1.0 mol dm^{-3} (2 cm^3)
- small lump of solid carbon dioxide (dry ice) and tongs, or a supply of carbon dioxide
- 250 cm^3 beaker

alkaline solution of glucose — IRRITANT

dilute ammonia solution — IRRITANT

ammonium vanadate(V) — TOXIC, IRRITANT

copper(II) ion — HARMFUL

lead nitrate(V) — TOXIC, OXIDISING

Methylene Blue indicator — HARMFUL

nickel(II) ion — HARMFUL

potassium chromate(VI) — VERY TOXIC

potassium hexacyanoferrate(II) — HARMFUL

potassium thiocyanate — HARMFUL

sodium hydroxide solution — IRRITANT

dilute sulphuric acid — IRRITANT

CARE Chromates(VI) irritate the eyes, the skin and the respiratory system. They are also suspected carcinogens. Avoid all skin contact and do not breathe any dust. Any spillage should be washed off at once.

CARE Eye protection and gloves must be worn.

WEAR EYE PROTECTION

WEAR PROTECTIVE GLOVES

* See instructions for preparation in the Teacher's and Technician's Guide

What you do

Investigate the following reactions, which all involve colour changes. In each case, record your observations and try to explain as far as possible what is happening to produce the colour change.

Doing all these reactions takes some time, so you will probably do only *one* of these. Show and explain this reaction to the other members of your class. In a similar way, go round the other members of your class and write down the observations they have made. Use textbooks to help where necessary. You will have met some of the reactions in earlier units (**From Minerals to Elements**, **The Atmosphere** and **The Steel Story**).

1 Place 100 cm^3 of an alkaline solution of glucose (**CARE** Irritant) in a 250 cm^3 bottle with a well-fitting stopper or rubber bung. Add enough Methylene Blue indicator (**CARE** Harmful) to give a good dark colour to the solution. (Methylene Blue is an indicator whose colour depends on the level of oxygen dissolved in the solution.)

Shake the bottle vigorously and leave it to stand. When the colour of the Methylene Blue has disappeared (this may take up to 30 minutes), shake the bottle again. You can repeat the process many times.

(You can vary the colour change by repeating the experiment and adding Phenolphthalein or Fluorescein as well as Methylene Blue.)

2 Place 10 cm^3 of acidified ammonium vanadate(V) solution (**CARE** Toxic and an irritant) into a boiling tube and add a piece of granulated zinc. Gently swirl and shake the tube until no further changes occur. You may need to heat the tube gently to speed up the reactions.

3 Heat a small sample of zinc oxide in a test-tube until there is no further change in colour. Stand the tube in a rack to cool. When cool, repeat the heating and cooling process.

4 Place a spatula-load of powdered lead nitrate(V) crystals into a test-tube. (**CARE** Lead nitrate(V) is toxic and oxidising. Use only a small amount and do not breathe the dust.) Add a spatula-load of powdered potassium iodide crystals. Cork the tube and shake it vigorously.

Repeat using dilute aqueous solutions of these two substances.

5 Investigate what happens when you add the reagent from list **A** to the metal ion solution opposite it in list **B** in Table 1. Use a teat pipette and shake the mixture after each addition. (**CARE** Copper(II) and nickel(II) salts are harmful.)

6 Add a few drops of Universal Indicator solution to some water in a beaker. Add enough dilute sodium hydroxide solution to raise the pH and give a deep purple colour. Now add a small lump of solid carbon dioxide (dry ice – **CARE** Dry ice should be handled with tongs), or bubble carbon dioxide from a generator through the solution.

7 Mix 2 cm^3 of lead nitrate(V) solution with 2 cm^3 of potassium chromate(VI) solution. (**CARE** Lead compounds are toxic and chromates(VI) are suspected carcinogens. Avoid all skin contact – wear gloves.) Put a drop of the resulting mixture on a slide and observe under a microscope.

Repeat the experiment but add a few drops of dilute sulphuric acid (**CARE** Irritant) to the potassium chromate(VI) solution before mixing.

A	B
sodium carbonate solution	$Cu^{2+}(aq)$
ammonia solution	$Cu^{2+}(aq)$
ammonia solution	$Ni^{2+}(aq)$
potassium hexacyanoferrate(II) solution, $K_4Fe(CN)_6$ (**CARE** Harmful)	$Fe^{3+}(aq)$
potassium (or ammonium) thiocyanate solution, KSCN (or NH_4SCN) (**CARE** Harmful)	$Fe^{3+}(aq)$

Table 1

Summary

At the end, draw up a summary table in which you classify each change occurring as one of the following:

- redox reaction
- ionic precipitation reaction
- acid-base reaction
- ligand exchange reaction
- polymorphic change.

(Compounds which can exist in more than one solid form, in which the ions or molecules are arranged in different ways, are said to be **polymorphic**.)

CD3

Seeing colours

In this activity you can examine the nature of the light reaching your eye from coloured solutions and from coloured surfaces.

Requirements

- hand-held direct-vision spectroscope (or diffraction grating)
- test-tubes and rack
- white light source or sunlight (an ordinary light bulb can be used, but it must be in a shade or a protective holder)
- aqueous solutions of a range of coloured compounds, for example:
  – copper(II) sulphate
  – chromium(III) chloride
  – potassium dichromate(VI)
  – screened Methyl Orange indicator
- protective gloves
- brightly coloured surfaces (such as exercise books or files)

CARE Dichromates(VI) irritate the skin and are suspected carcinogens. Avoid all skin contact. Any spillage should be washed off at once. Wear protective gloves.

chromium(III) chloride

copper(II) sulphate

potassium dichromate(VI)

CARE Eye protection and gloves must be worn.

What you do

Point the spectroscope at a window or source of white light and observe the effect it has on the light. (You may wish to use a diffraction grating instead of a spectroscope.)

Investigate the effect of placing a coloured solution between the white light source and the spectroscope, as shown in Figure 1. Summarise your observations in a table.

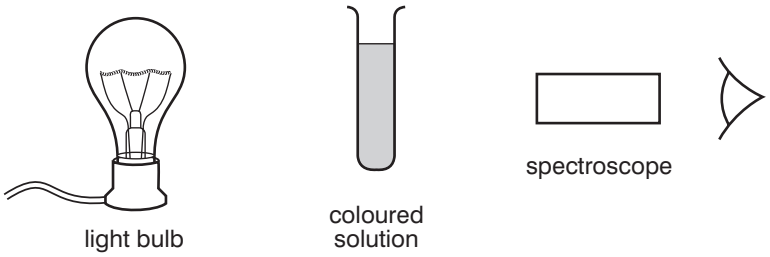


Figure 1 Investigating the effect of coloured solutions on white light

Now point the spectroscope at a well-lit brightly coloured surface such as an exercise book or file. You may want to read **Chemical Ideas 6.7** to help you explain your observations.

QUESTIONS

a What effect does the spectroscope have on white light?

b Describe what you observed when a coloured solution was placed between the white light source and the spectroscope. Explain why this happens.

c Use your observations with coloured surfaces to help you write a short explanation of why paintings appear coloured when you look at them with the naked eye.

CD4.1

Using reflectance spectra to identify pigments

***In this activity you will use reflectance spectra to find out which pigments Cima used 500 years ago to produce two different areas of blue in his altarpiece* The Incredulity of S. Thomas.**

Reflectance spectra

The surface of a painting is not smooth and light is reflected from it in all directions.

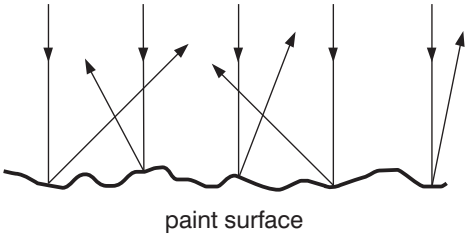


Figure 1 The reflection of light from a paint surface

A reflectance spectrum tells you how much light of each colour in the spectrum is reflected in a particular direction.

The reflectance spectrum of a painting is obtained by shining light on a small area and analysing the light reflected off the surface of the pigments at a particular angle.

Figure 2 shows a simplified version of the apparatus used. The monochromator contains a prism which splits the white light into its component wavelengths. The prism is rotated so that the wavelength of the light focused on the painting can be varied. The apparatus also incorporates a camera which takes a photograph of the precise spot on the painting that is being examined.

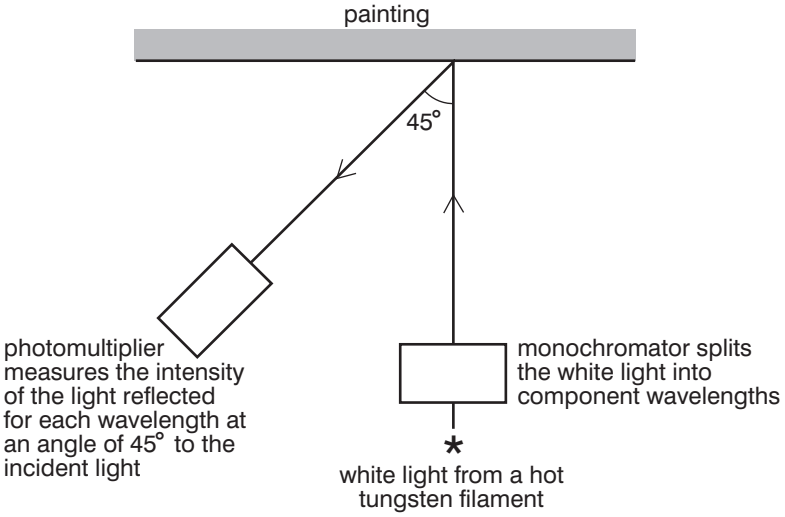


Figure 2 Obtaining the reflectance spectrum of a sample of paint

What you do

Below are the reflectance spectra of two blue pigments used by Cima. They were taken from two different parts of the painting, area A and area B (see Figures 3 and 4). The horizontal axis represents the wavelengths of the light reflected. The vertical axis shows the percentage of the incident light reflected by the pigment.

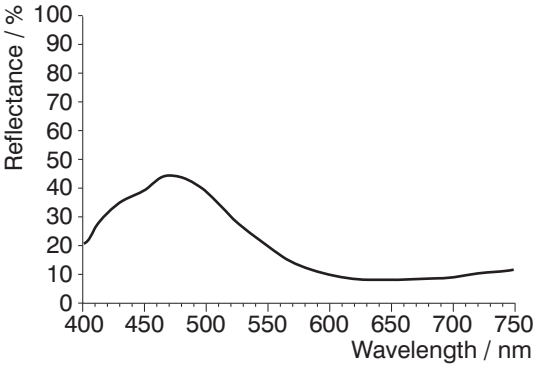


Figure 3 Reflectance spectrum of area A

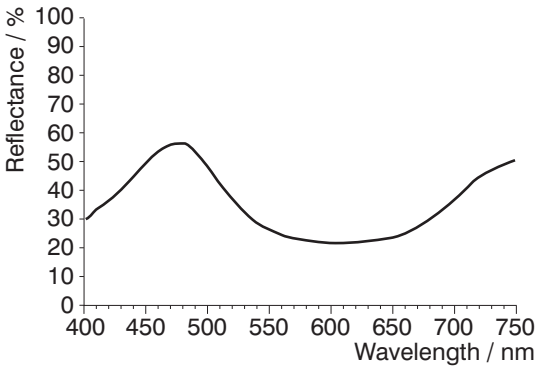


Figure 4 Reflectance spectrum of area B

Study the reflectance spectra in Figures 3 and 4 and then compare them with the reflectance spectra of some traditional blue pigments which were in use at the time Cima was painting the altarpiece. These are shown on **Information Sheet 1** *(Traditional blue pigments)*.

QUESTIONS

a Which blue pigments do you think are present in the paint areas A and B?

b What is the chemical composition of each of these pigments?

c How would you expect the *shade of blue* to differ for the two pigments? (You may want to look at your **Data Sheets** to find out which colours correspond to the various wavelengths in the visible spectrum.)

d Look at Cima's *The Incredulity of S. Thomas* (**Storyline CD4,** Figure 13). Look carefully at the different blue areas in the picture. In which part of the painting do you think Cima might have used these pigments?

e Why do you think it is important to take a photograph of the precise spot on the painting that is being subjected to measurement?

f How might reflectance spectra provide information on the effect of gallery lights on various pigments?

Information Sheet 1: Traditional blue pigments

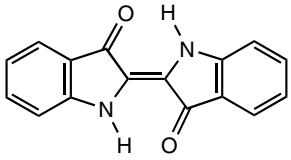
Pigment	Source	Chemical composition
Smalt	Zaffre (cobalt arsenate)	Blue glass pigment made by melting cobalt arsenate with sand and K_2CO_3
Azurite	Azurite	$2CuCO_3.Cu(OH)_2$
Natural Ultramarine	Lapis lazuli	A sodium aluminium silicate containing sulphur
Indigo	Vegetable dye extracted from woad or from the *Indigofera tinctoria* plant	

Table 1 Information about some traditional blue pigments in use in the early 16th century

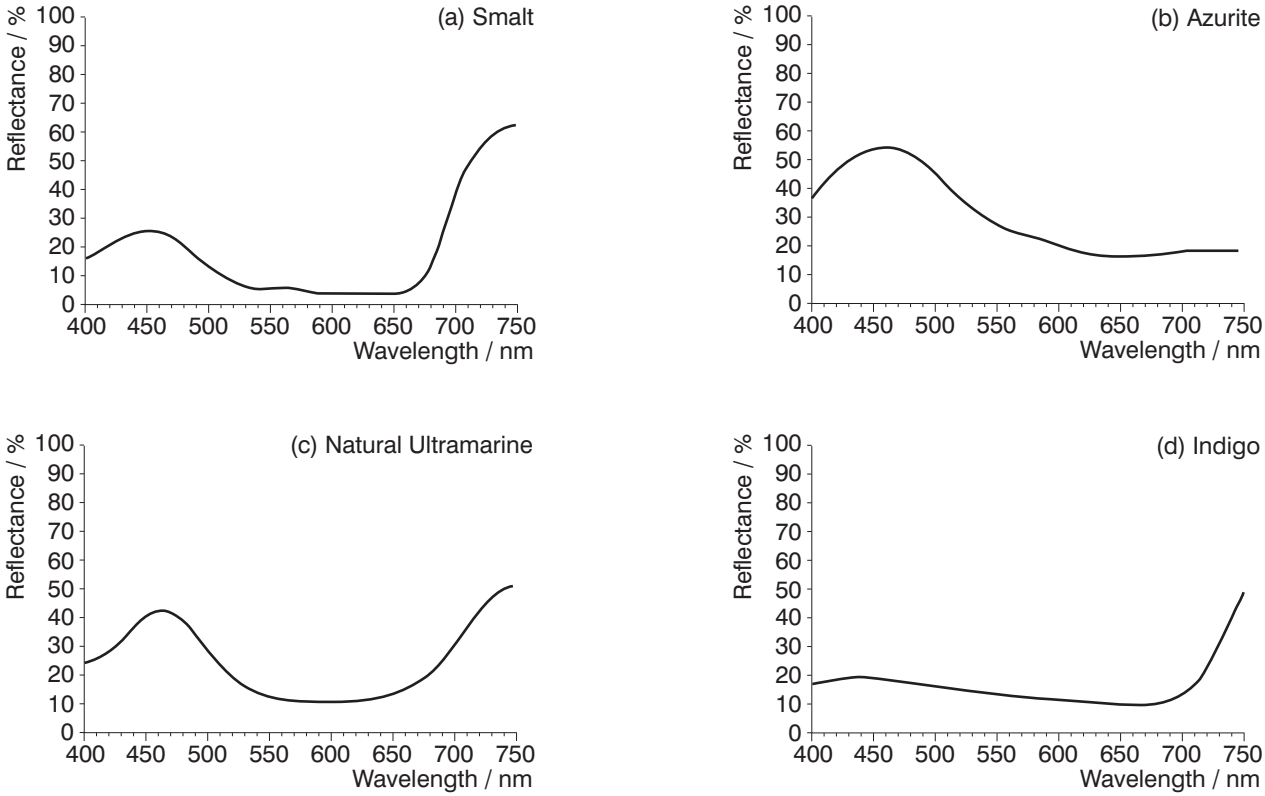


Figure 1 Reflectance spectra for four traditional pigments

CD4.2

What factors affect the drying potential of an oil?

In this activity you will use information from experiments to decide what factors affect the drying potential of an oil. You can then make some deductions about the complex chemistry of the drying process.

Different types of oil

If a **drying oil** is exposed to air, it eventually becomes a rubbery solid. If only a thin layer is exposed, it becomes hard. **Non-drying oils** do not harden in this way, but they may thicken on heating. In between the two extremes are the **semi-drying oils**. These thicken and form a skin when exposed to air at high temperatures.

Only drying oils are suitable for mixing with pigments to make paints.

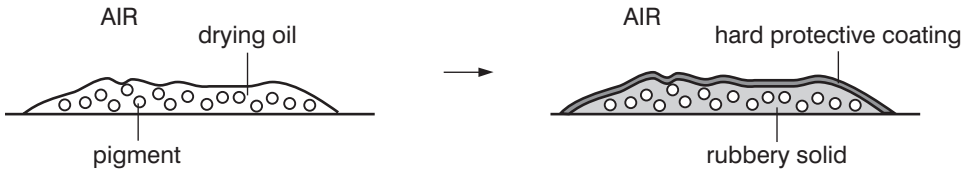


Figure 1 The action of air on an oil-based paint

Paint layers dry from the outside to give a tacky surface first; eventually they become hard throughout. The drying process is irreversible.

Iodine numbers

Natural oils can be classified according to their **iodine number**. This is calculated on the basis of how much iodine(I) chloride (ICl) will react with the oil. The more ICl reacts with the oil, the higher the iodine number. Table 1 gives the iodine numbers for some natural oils.

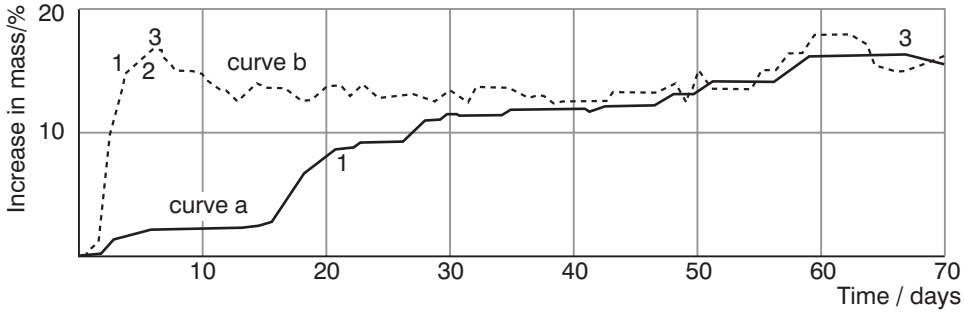
Oil	Drying potential	Iodine number
linseed	drying	170–195
poppy	drying	140–158
walnut	drying	140–150
almond	non-drying	<100
olive	non-drying	<100
castor	non-drying	<100
cotton-seed	semi-drying	103–111
maize	semi-drying	117–130
sesame	semi-drying	100–120

Table 1 Information about some natural oils

A closer look at linseed oil

Figure 2 shows the results of an experiment to investigate the drying of linseed oil. It shows the percentage increase in mass of two samples plotted against the drying time in days. The linseed oil samples were left exposed to the air and were kept at a constant room temperature.

Figure 2 The drying of linseed oil. Curve a is for a film of linseed oil prepared and dried in the dark, and weighed under red light. Curve b is for an identical film of linseed oil prepared, dried and weighed in diffuse daylight. 1 = point of initial set; 2 = tacky stage; 3 = tack-free dryness.



No significant increase in mass was observed if the linseed oil samples were kept in an atmosphere of nitrogen.

QUESTIONS

a How is the drying potential of an oil related to its iodine number?

b Look at the structures of some of the carboxylic acid components of the triesters found in natural oils. You can find these in **Chemical Ideas 13.6**. With which structural feature of these molecules do you think ICl will react? What *type* of reaction is involved?

c Which parts of the triester molecules in natural oils do you think are involved in the drying process?

d What other substance seems to be involved in the drying reaction? Explain your answer.

e Suggest what type of chemical processes might be involved when natural oils harden.

f What experiments would you want to do to confirm your suggestions?

g Explain how the drying of an oil paint is different from the drying of watercolours.

CD4.3

Investigating paint media

***In this activity you will analyse gas-liquid chromatograms to find out which oil was used as the binding medium for Cima's paints in* The Incredulity of S. Thomas.**

The problem

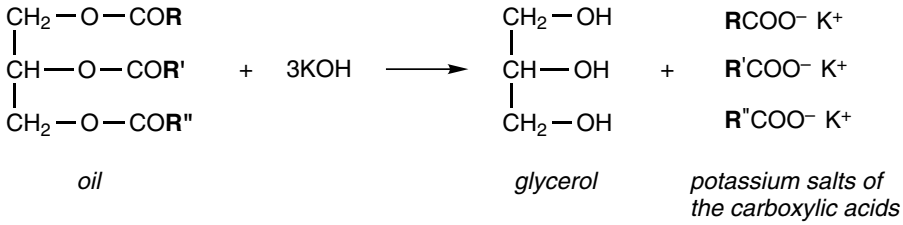
Oils are triesters of glycerol with long-chain carboxylic acids (see **Chemical Ideas 13.6**). Different oils contain different amounts of each acid, and the ratio of the acids can be characteristic of a particular oil.

The trouble is that the cross-linking process which causes paint to dry involves the *unsaturated* carboxylic acid chains, and this polymerisation is irreversible. So, when chemists analyse samples of paint, they measure the ratio of two *saturated* carboxylic acids, since these are not involved in the cross-linking. The acids chosen are *palmitic acid* and *stearic acid*. Their ratio is unchanged by the drying process.

Analysing a sample of paint

A small sample of paint, about the size of a pin head, is removed from the painting and treated to make it suitable for analysis by gas-liquid chromatography (g.l.c.).

First, the paint sample is warmed in potassium hydroxide solution to hydrolyse the ester links in the oil. Potassium salts of the carboxylic acids are produced:

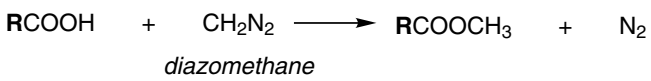


oil *glycerol* *potassium salts of the carboxylic acids*

The groups **R**, **R'** and **R"** vary according to the carboxylic acid present (for palmitic acid, for instance, **R** is $CH_3(CH_2)_{14}$).

The mixture is now acidified with hydrochloric acid to liberate the free carboxylic acids. These will be simple fatty acids as well as acids of the polymeric cross-linked material. Stearic acid and palmitic acids are among the fatty acids produced:

The free acids are not very volatile and are difficult to analyse using g.l.c. (They take a long time to emerge from the column and do not produce sharp peaks.) The next stage is therefore to convert the acids to their more volatile methyl esters. Because of the very small quantities involved, a powerful methylating agent called *diazomethane* is used:



It is this mixture of methyl esters which is injected onto the column of the gas-liquid chromatograph. (You can find out how a gas-liquid chromatograph works in **Chemical Ideas 7.6**.)

Figure 1 shows the chromatogram obtained when a small sample of paint from Cima's altarpiece was treated in this way.

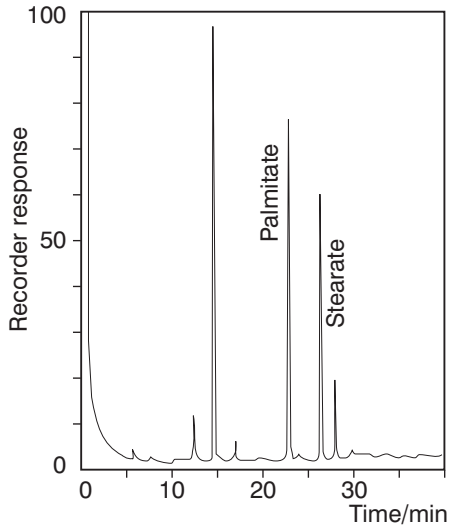


Figure 1 Gas-liquid chromatogram of a sample made from paint from Cima's The Incredulity of S. Thomas.

What you do

Use the information on **Information Sheet 2** *(Gas-liquid chromatograms)* to help you analyse the chromatogram in Figure 1. (The same conditions were used to obtain all the chromatograms.)

First, identify the peaks due to the palmitate and stearate esters, and then work out the palmitate : stearate ratio in the sample. The peaks are very sharp so you can assume that the peak height is proportional to the amount of compound present. (Strictly speaking, you should measure the *area* under each peak.)

Now work out the palmitate : stearate ratios for each of the reference samples, from paint made up in known oils. Compare these ratios with the value you obtained for the sample from Cima's paints.

QUESTIONS

a Which oil do you think was used to bind Cima's paints in 1504? Explain your answer.

b Explain why the palmitate:stearate ratio is the one chosen for analysis.

c Suggest why methyl esters are more volatile than the free carboxylic acids.

d Give another method for converting palmitic acid to its methyl ester. Write a balanced equation for the reaction.

Information Sheet 2: Gas-liquid chromatograms

The conditions used during analysis, the type of chromatography column and detector, the temperature and the flow rate of the carrier gas, were the same in each case. A hydrocarbon with a high relative molecular mass was used as the stationary phase in the column.

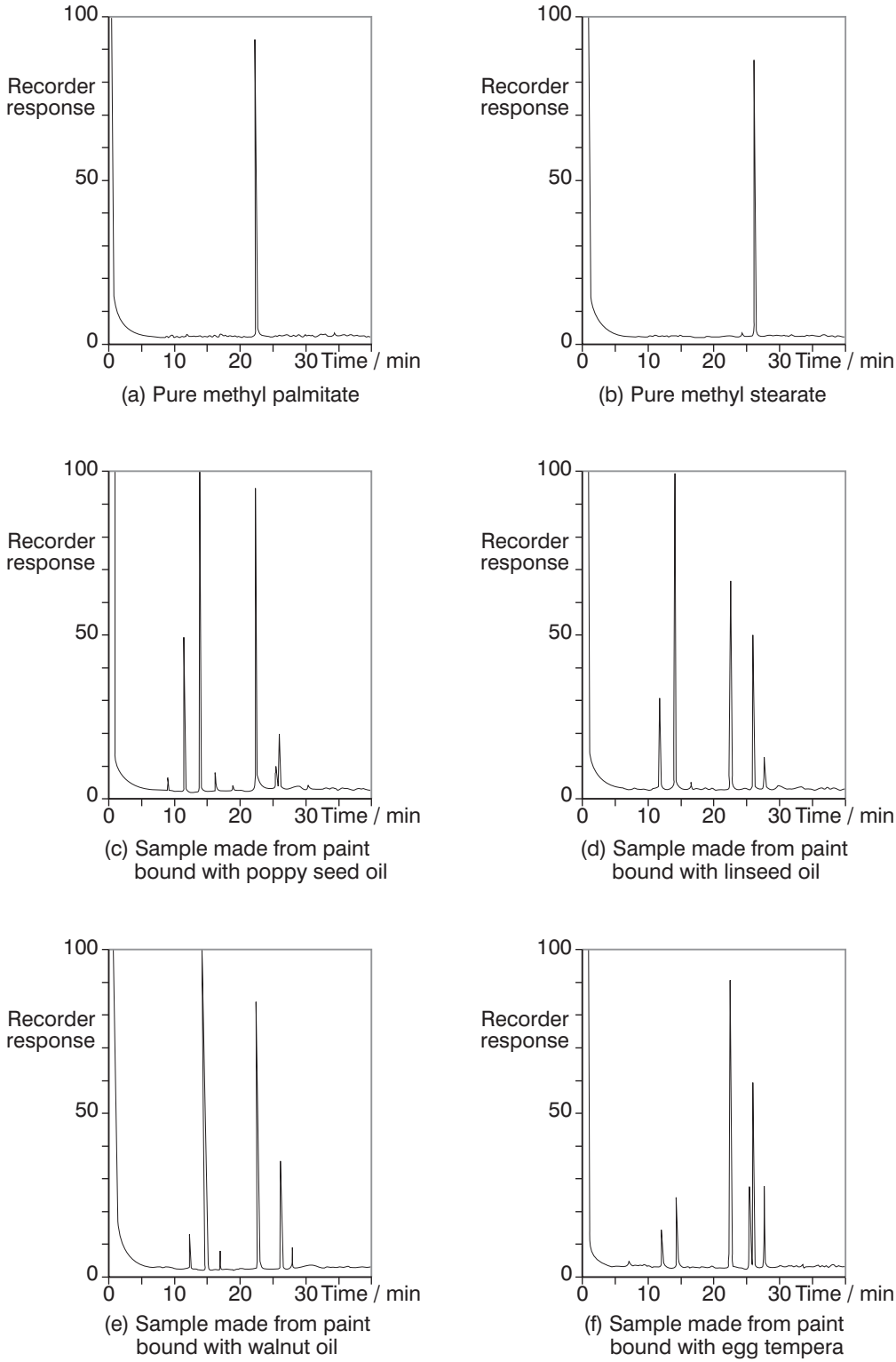


Figure 2 Gas-liquid chromatograms of: (a) pure methyl palmitate; (b) pure methyl stearate; (c–f) samples made from paint bound with poppy seed oil, linseed oil, walnut oil and egg tempera, respectively.

CD4.4

Identifying a pigment

***In this activity you can combine evidence from scientific and historical sources to identify the yellow-orange pigment Cima used for the robe of S. Peter in his painting* The Incredulity of S. Thomas.**

What you do

Your task is to identify the yellow-orange pigment used for the robe of S. Peter. You will use the kind of scientific results and historical information that scientists and art historians at the National Gallery in London had at their disposal when analysing the painting. (S. Peter is the Apostle with the white hair and a beard, standing in the foreground next to Christ on the right-hand side of the picture.)

Photomicrograph of a cross-section of paint

A diagram of this is shown in Figure 1. You may be able to see a coloured slide of it. (A **photomicrograph** is a picture taken under a microscope.)

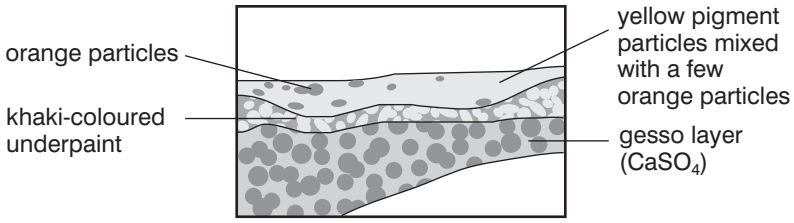


Figure 1 Diagram of the photomicrograph of a cross-section of paint taken from the robe of S. Peter (× 120)

Historical evidence

Information Sheet 3 *(Background information on some yellow pigments)* gives some historical information about the use of yellow and orange pigments. These extracts are taken from a standard textbook on painting materials. Such information is always used in addition to the results of any scientific analysis.

LMA emission spectrum

The **emission spectrum** from the paint sample consists of a series of lines. It is projected onto a reference spectrum in a special apparatus. The elements present in the sample are then identified by matching the lines to those on the reference spectrum.

The LMA emission spectrum of the yellow-orange pigment from S. Peter's robes showed characteristic lines at 228.8 nm and 235.0 nm. You can see a small section (from 223 nm to 252 nm) of the reference spectrum in Figure 1 on **Information Sheet 4** (*Reference emission spectrum for LMA spectra*). The apparatus at the National Gallery could detect light emitted between 220 nm and 460 nm (i.e. ultraviolet and visible light) so the whole reference spectrum is very long!

Summary

Write a *short* report summarising your findings. Which pigment do you think Cima used? Give reasons for your decision.

Information Sheet 3: Background information on some yellow pigments

Barium Yellow This is barium chromate(VI), $BaCrO_4$. It is a pale green-yellow pigment made by mixing neutral solutions of potassium chromate(VI) and barium nitrate(V). It may become slightly greener on exposure to light due to formation of chromium(III) oxide. The metal chromium was discovered by Vauquelin in 1797 and he described the preparation of barium chromate(VI) in 1809.

Cadmium Yellow This is cadmium sulphide, CdS, which is prepared by precipitation from an acid solution of a soluble cadmium salt (chloride or sulphate) with hydrogen sulphide or an alkali metal sulphide. The colour of pure cadmium sulphide ranges from lemon yellow to deep orange, depending on the way it is prepared. Cadmium sulphide exists naturally as the mineral *Greenockite,* but the use of the mineral as a pigment has not been recorded.

The first chemical preparation of cadmium sulphide seems to have been by Stromeyer in 1817. It is now perhaps the most important yellow pigment in the artist's palette, though there are increasing concerns about its toxic nature.

Chrome Yellow (See **Storyline CD3**.) This is lead chromate(VI), $PbCrO_4$. It is a bright yellow pigment made by mixing solutions of potassium chromate(VI) and lead nitrate(V). Vauquelin described its preparation by this method in 1809; a range of different shades of yellow may be produced depending on the conditions.

Indian Yellow This is a yellow organic extract introduced in the 15th century. It was prepared at Monghyr in Bengal from the urine of cows fed on mango leaves. Its manufacture by this method is now prohibited by law. It has a deep, rich, translucent, orange colour. This pigment was used in India in the manufacture of paint because of its resistance to fading when exposed to light. The colour sold under this name today is a synthetic substitute.

Lead-Tin Yellow X-ray crystallography has shown this pigment to be an artificially produced compound of the oxides of tin and lead containing silicon as an essential constituent, $PbSnSiO_3$.

Recipes in the Bolognese Manuscript of the early 15th century note the manufacture of 'yellow glass for beads' involving heating lead and tin together in a furnace, followed by a second stage to produce a pigment for painting. Lead-Tin Yellow was used extensively in Venetian 16th century painting and continued to be used into the mid-17th century.

Naples Yellow This is lead antimonate. It may be considered to be chemically combined lead and antimony oxides, $Pb_3(SbO_4)_2$. It varies in colour from sulphur-yellow to orange-yellow. Recipes for it first appeared in the 18th century.

Orpiment This was once widely used as a pigment, particularly in the East, but has now fallen into complete disuse because of its limited supply and its poisonous nature. It is the yellow sulphide of arsenic, As_2S_3, occurring naturally in many places but not in large quantities. Orpiment is brilliant when pure, with a rich lemon-yellow tone. It is mentioned as a pigment in 14th and 15th century Italy, and although quite rare elsewhere, it is characteristic of many 16th century Venetian paintings.

Realgar This is a natural orange-red sulphide of arsenic, As_2S_2, and is closely related chemically to Orpiment. The two minerals are often found together in the same deposits. Like Orpiment it was known in ancient times.

Yellow Ochre An *ochre* is a natural earth pigment which consists of a mixture of silica and clay. It owes its colour to the presence of iron(III) oxide, Fe_2O_3. In Yellow Ochre, the colour is caused by the presence of various hydrated forms of the oxide. Yellow Ochre has been used universally as a pigment from earliest history. It was known and used in ancient Egypt, in Roman times and in the East. It was important in the Middle Ages and in all periods of European painting.

Information Sheet 4: Reference emission spectrum for LMA spectra

The reference spectrum is an emission spectrum of iron which has many lines throughout the 200 nm–460 nm range. The full reference spectrum is very long and has marked on it the positions of the characteristic lines of around 60 elements.

Below is a small section of the reference spectrum, between 223 nm and 252 nm.

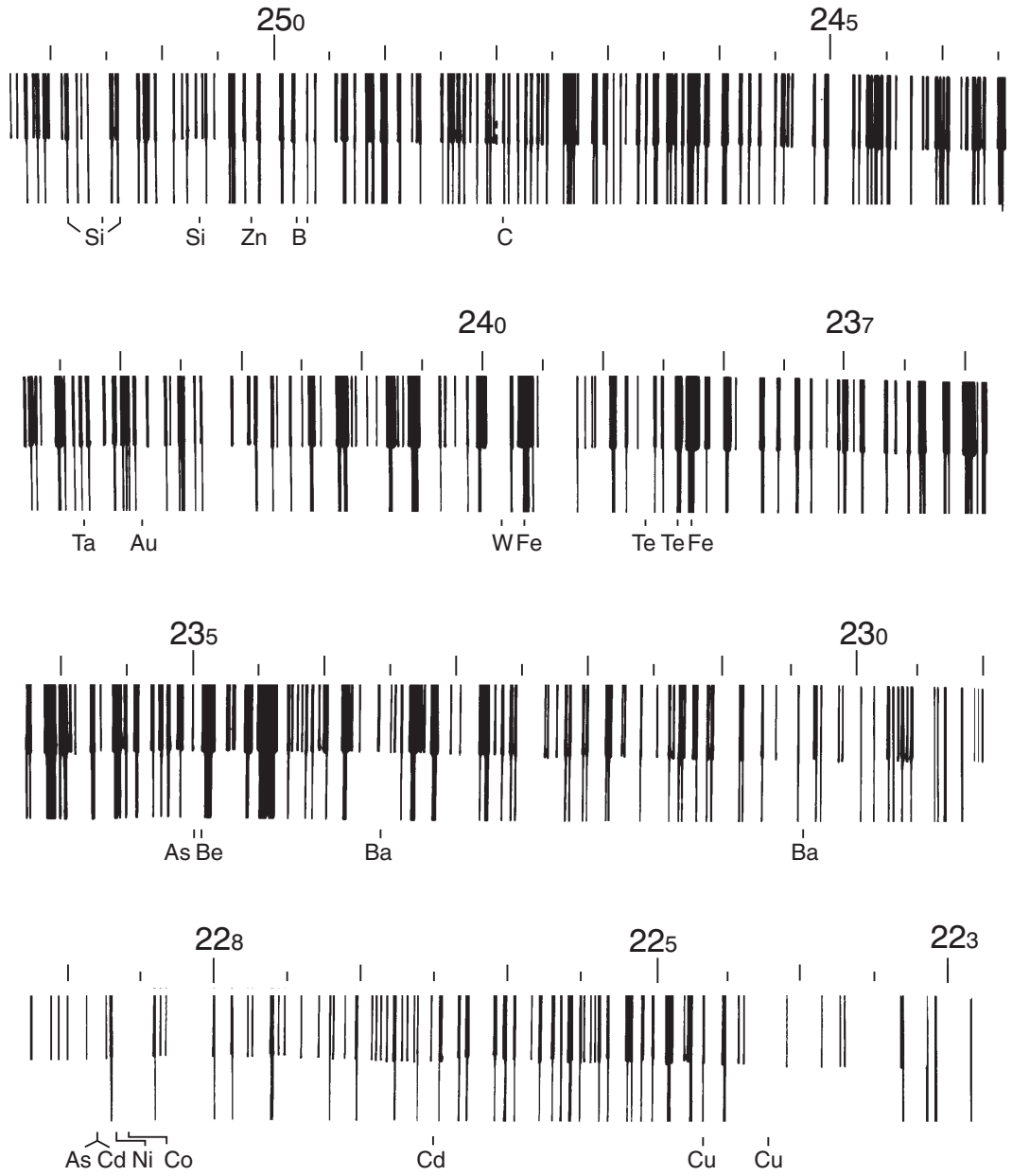


Figure 1 A small section (from 223 nm to 252 nm) of the reference spectrum for use with LMA emission spectra of pigments. (The upper spectrum is a spark spectrum; the lower one an arc spectrum.)

CD4.5

Finding a perfect match

***In this activity you will use reflectance spectra to find modern replacements for two blue pigments used in Cima's* The Incredulity of S. Thomas.**

Why use modern pigments?

Why don't restorers simply use the original pigments once these have been identified?

Restorers may substitute modern pigments for several reasons. It may be that the original pigment is not available, or that the modern version of it is not quite the same. Immense care was taken with the preparation of pigments in the workshops of Renaissance artists. The chemically equivalent pigments available today rarely give as intense a colour. In addition, the original pigment may have changed colour with age.

Modern pigments are readily available. They are usually more stable and less toxic than their traditional counterparts.

Although it is often possible to match a modern colour exactly to that of a faded original pigment, it is not possible to ensure that the two pigments will change in the same manner in the future. There is no point in achieving a perfect match with an old pigment only to see the retouching fade. One solution is to keep the restored painting in a carefully controlled environment, so that all further change is kept to a minimum.

What you do

Imagine you are a scientist working in the Scientific Department at the National Gallery. You have just received a memo from the Conservation Department asking you to recommend the best blue pigments for use in the restoration of two areas of Cima's altarpiece:

- the blue-green areas of the ceiling
- the dark blue mantle of the Apostle on the extreme left of the group.

You have already supplied the Department with the identity of the original pigments used by Cima (look back to **Activity CD4.1**). Now you need to find the best modern substitutes.

The reflectance spectra of some modern blue pigments are shown on **Information Sheet 5** (*Some modern blue pigments*). Use these spectra to help you construct a reply to the Conservation Department. Outline the reasons for your recommendations.

Information Sheet 5: Some modern blue pigments

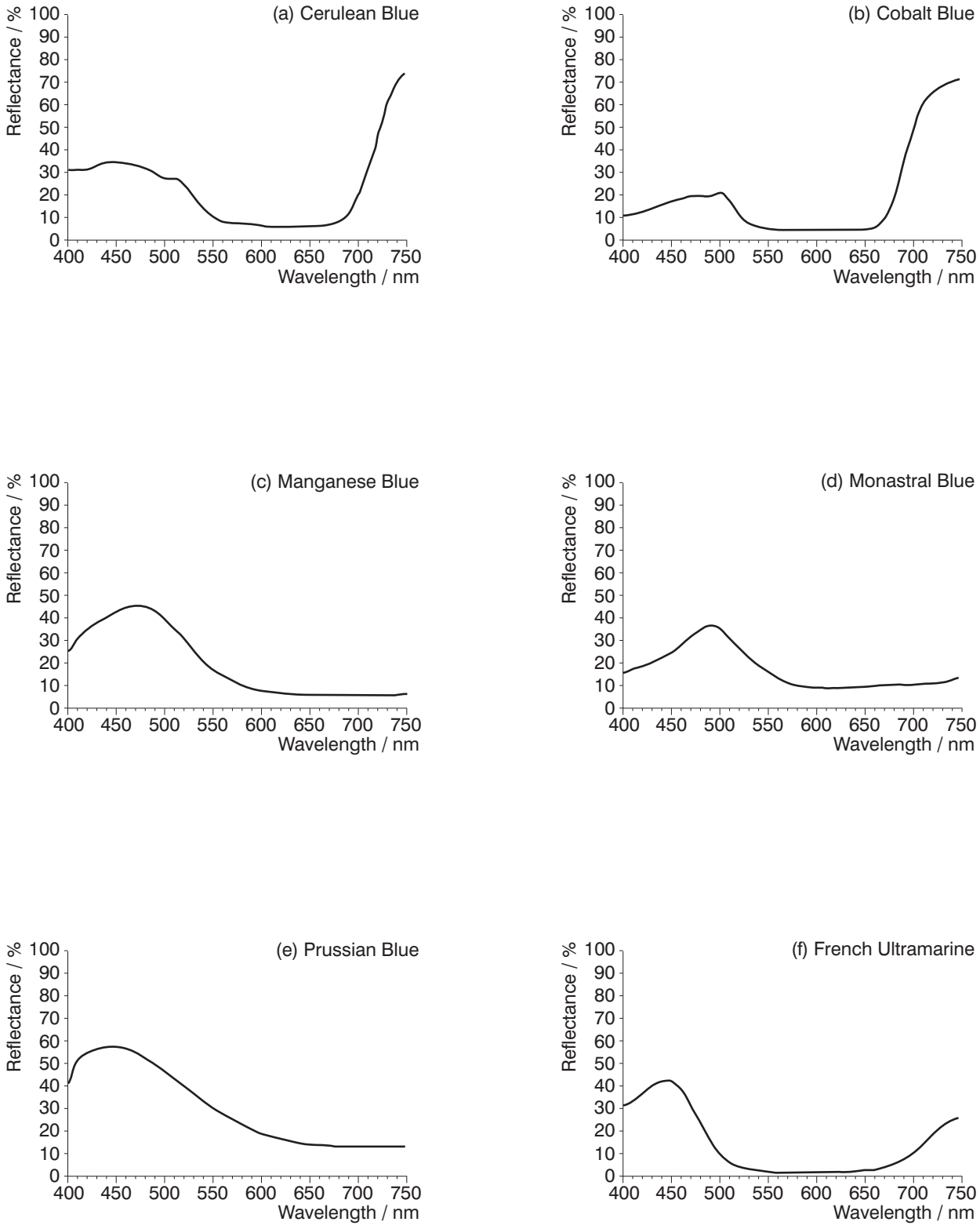


Figure 1 Reflectance spectra of some modern blue pigments

CD5

Comparing hydrocarbons

The purpose of this activity is to compare the behaviour of three liquid hydrocarbons – cyclohexane (an alkane), cyclohexene (an alkene) and methylbenzene (an arene) – with a series of chemical reagents.

Requirements

- test-tubes and rack
- bungs
- boiling tube
- teat pipettes
- cyclohexane (2 cm^3)
- cyclohexene (2 cm^3)
- methylbenzene (2 cm^3)
- bromine in cyclohexane solution (3 cm^3)
- glass rod
- concentrated ammonia solution (2 cm^3)
- bromine water (6 cm^3)
- concentrated nitric acid (2 cm^3)
- concentrated sulphuric acid (fresh) (7 cm^3)
- dilute sulphuric acid, 1.0 mol dm^{-3} (20 cm^3)
- dilute potassium manganate(VII) solution, 0.02 mol dm^{-3} (3 cm^3)
- potassium manganate(VII) crystals (0.5 g)
- solid sodium carbonate (0.05 g)
- sodium disulphite(IV) (metabisulphite) solution, 1.0 mol dm^{-3} (5 cm^3)
- 250 cm^3 beaker
- 10 cm^3 measuring cylinder
- 100 cm^3 conical flask
- 0–110 °C thermometer
- source of hot water
- crushed ice (50 g)
- methyl benzoate (2.5 cm^3)

CARE Cyclohexane, cyclohexene and methylbenzene are highly flammable liquids. Keep bottles stoppered when not in use and well away from naked flames. Avoid skin contact and do not breathe the vapours.

CARE Bromine is corrosive, causes severe burns and gives off a toxic vapour. Handle the bromine solution with care. Measure out in a fume cupboard using a marked pipette.

CARE Solid potassium manganate(VII) is a powerful oxidising agent. It causes staining of skin and clothes. Wear protective gloves if necessary.

CARE Eye protection must be worn.

bromine — TOXIC; CORROSIVE

bromine water — IRRITANT

concentrated ammonia solution — CORROSIVE

concentrated nitric acid — CORROSIVE; OXIDISING

concentrated sulphuric acid — CORROSIVE

cyclohexane — HIGHLY FLAMMABLE

cyclohexene — HIGHLY FLAMMABLE

dilute sulphuric acid — IRRITANT

methylbenzene — HARMFUL; HIGHLY FLAMMABLE

methyl benzoate — HARMFUL

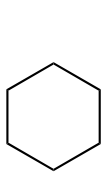
potassium manganate(VII) crystals — HARMFUL; OXIDISING

sodium carbonate — IRRITANT

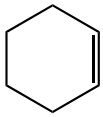
sodium disulphite(IV) solution — HARMFUL

Introduction

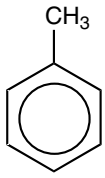
Arenes have characteristic properties which are very different from those shown by alkanes and alkenes. In this activity you will compare the reactions of cyclohexane (an alkane), cyclohexene (an alkene) and methylbenzene (an arene). (Benzene itself is toxic and has carcinogenic properties, so it cannot be used.)



cyclohexane



cyclohexene



methylbenzene

What you do

For each of the test-tube reactions, use just a *few drops* of each of the hydrocarbons.

In each case, think first what you expect to happen and why. Then compare this with what you actually observe.

Describe what happens in each case. Write equations where appropriate, and name the products of any reactions. It may be best to draw up tables for your results. You may wish to consult **Chemical Ideas** Chapter 12 to help you interpret your observations.

Classify the *type* of reaction occurring, choosing words from the list below:

substitution	nucleophilic
addition	electrophilic
oxidation	radical

1 Reaction with bromine

1 For each hydrocarbon in turn (**CARE** Highly flammable liquids with harmful vapours), place a few drops in a test-tube and add 1 cm^3 of a solution of bromine in cyclohexane (**CARE** Corrosive and gives off a toxic vapour). Stopper the tubes and shake them thoroughly. Test any gases given off by holding a drop of ammonia solution (**CARE** Corrosive) on a glass rod at the mouth of the test-tube.

2 Repeat the tests in step **1**, but this time add a few cm^3 of bromine water (**CARE** Irritant) to each tube.

2 Reaction with potassium manganate(VII)

3 Mix 3 cm^3 dilute sulphuric acid (**CARE** Irritant) and 3 cm^3 dilute potassium manganate(VII) solution in a test-tube.

Add 1 cm^3 of the above solution to a few drops of each hydrocarbon in separate test-tubes. Stopper the tubes and shake them thoroughly.

If no reaction occurs, carefully warm the tube (by placing it in a beaker of warm water) and then leave it to stand.

4 Investigate the reaction with methylbenzene further, as follows. Put 5 drops of methylbenzene (**CARE** Highly flammable liquid with harmful vapour), 5 cm^3 of water, 0.05 g of solid sodium carbonate (**CARE** Irritant) and 0.5 g of potassium manganate(VII) crystals (**CARE** Powerful oxidising agent, harmful) into a boiling tube.

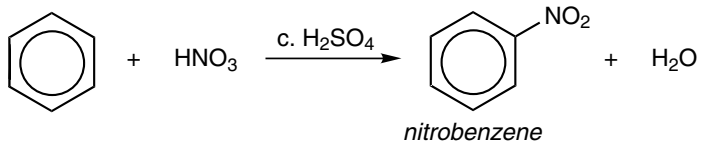
Clamp the tube in a near-vertical position and lower it into a beaker of water. Heat the water until the contents of the boiling tube start to reflux. Continue heating gently until the purple colour of the manganate(VII) ions disappears. (Alternatively, a small-scale reflux apparatus with a pear-shaped flask and a water condenser could be used. The flask could be carefully heated with a small Bunsen flame.)

Cool the mixture and then acidify by adding dilute sulphuric acid (**CARE** Irritant). Add sodium disulphite(IV) (metabisulphite) solution (**CARE** Harmful) to remove the brown manganese(IV) oxide.

Use a textbook to find out the name of the white crystals formed, and to help you explain what has happened.

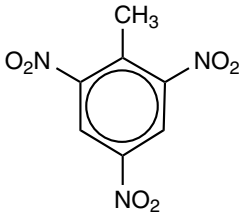
3 *Nitration of methyl benzoate*

One of the most important reaction of arenes is **nitration**. For example:

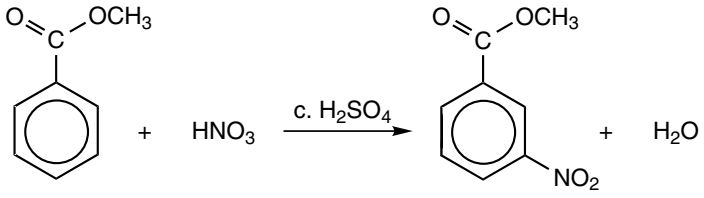


nitrobenzene

The nitro-derivatives of methylbenzene can be explosive. For example:



is trinitrotoluene (TNT; toluene is the old name for methylbenzene). A safer compound to nitrate is methyl benzoate:



methyl benzoate *methyl 3-nitrobenzoate*

5 Measure 2.5 cm^3 of methyl benzoate (**CARE** Harmful) into a small conical flask and then add 5 cm^3 of concentrated sulphuric acid (**CARE** Corrosive). When the liquid has dissolved in the acid, cool the mixture in ice.

Prepare the *nitrating mixture* by carefully adding 2 cm^3 of concentrated sulphuric acid (**CARE** Corrosive) to 2 cm^3 of concentrated nitric acid (**CARE** Corrosive; oxidising agent). Cool the mixture in ice during the addition.

Now add the nitrating mixture drop by drop from a teat pipette to the solution of methyl benzoate while cooling. (Do not allow the nitrating mixture to get into the rubber teat.)

Stir the mixture with a thermometer and keep the temperature below 10 °C. When the addition is complete, allow the mixture to stand at room temperature for another 15 minutes.

After this time, pour the reaction mixture onto about 25 g of crushed ice and stir until the ice has melted.

QUESTIONS

a You used cyclohexane and cyclohexene as examples of a typical alkane and alkene respectively. Why weren't simpler hydrocarbons such as ethane and ethene used?

b In the reactions with bromine water and acidified potassium manganate(VII) solution, why was it necessary to shake the tubes thoroughly?

c How would you expect benzene to react with an acidified solution of potassium manganate(VII)? Explain your answer.

d **i** In the nitration of methyl benzoate, what precautions were taken to help prevent further nitration to a dinitro-derivative?

ii Give the names and structural formulae of two nitro-compounds that are likely to contaminate the crystals of methyl 3-nitrobenzoate that you made.

iii Suggest how you could purify your crystals and confirm that they are crystals of methyl 3-nitrobenzoate.

CD6

Making azo dyes

In this activity you can investigate the range of colours which can be obtained by making azo dyes with different coupling agents.

Requirements

- boiling tubes
- test-tube and rack
- bungs
- protective gloves
- 10 cm^3 measuring cylinder
- phenylamine (1.5 cm^3)
- ethyl 4-aminobenzoate (benzocaine) (2 g)
- dilute hydrochloric acid, 1.0 mol dm^{-3} (10 cm^3)
- 250 cm^3 beaker
- ice-salt mixture
- 0–110 °C thermometer
- sodium nitrite (nitrate(III)) (2 g)
- glass rod
- starch-iodide paper
- dilute sodium hydroxide solution, 2.0 mol dm^{-3} (6 cm^3)
- small quantities of each of the following coupling agents:
  – phenol
  – methylphenol (any isomer)
  – naphthalen-2-ol

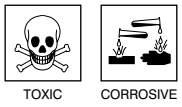
CARE Work in a fume cupboard when measuring out phenylamine.

CARE Phenol and methylphenols are toxic and corrosive. Wipe up any crystals that get spilt.

CARE Only *small amounts* of the azo dyes should be made. They should be disposed of promptly by flushing down the sink with lots of water and detergent.

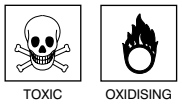
methylphenol 

naphthalen-2-ol 

phenol 

phenylamine 

sodium hydroxide solution 

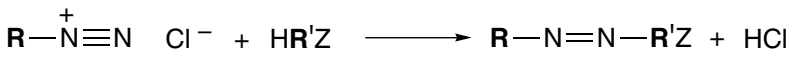
sodium nitrite 

CARE Eye protection must be worn. 

CARE Wear gloves throughout this experiment. Avoid all skin contact with the reagents and the azo dyes produced. 

Azo dyes

Azo dyes are produced in a **diazo coupling** reaction. For example,



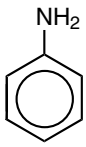
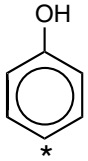
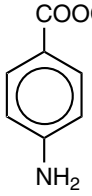
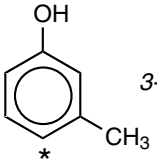
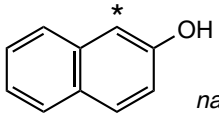
where **R** and **R'** are arene groups and **Z** is a functional group such as –OH or $–NH_2$. When **Z** is an –OH group, the coupling agent is prepared in alkaline solution.

Many modern azo dyes are formed directly on the fibres. First the cotton material is dipped into a solution of the coupling agent. The material is almost colourless at this stage. Next the cotton is treated with an ice-cold solution of a diazonium salt made from an arylamine. The insoluble dye is trapped in the fibres.

What you do

Your group will work as a 'development team'. You will prepare a series of azo dyes with different R'Z groups to investigate the range of colours that can be produced.

This means that you will use the same diazonium salt in each reaction and vary the coupling agent. You can select your amine RNH_2 to make the diazonium salt, and the coupling agents (HR'Z) from those in the table below.

Amines (RNH_2)	Coupling agents (HR'Z)
 *phenylamine*	 *phenol*
 *ethyl 4-aminobenzoate (benzocaine)*	 *3-methylphenol*
 *naphthalen-2-ol*	

* *indicates the position where coupling is most likely to occur*

Making the diazonium salt

1. First make a stock solution of a diazonium salt. Measure out your chosen amine (RNH_2) into a boiling tube. Use 0.15 cm^3 (about 2–3 drops) of phenylamine (**CARE** Toxic) or 0.25 g of benzocaine. Add 10 cm^3 of dilute hydrochloric acid and swirl the solution to ensure mixing.
2. Cool the solution by placing the tube in a beaker containing an ice-salt mixture, until the temperature of the solution is just below 5 °C. (If the temperature falls too low, the contents of the tube will freeze.)
3. Meanwhile, prepare a solution of 2 g of sodium nitrite (nitrate(III)) (**CARE** Toxic; oxidiser) in 10 cm^3 of water in another boiling tube. Swirl to ensure mixing and cool this solution to 5 °C.
4. Add the sodium nitrite solution *slowly* to the amine salt solution with stirring, taking care that the temperature does not rise above 5 °C. Continue adding the sodium nitrite solution until the mixture gives an instantaneous blue-black colour when spotted on starch-iodide paper. This indicates that diazotisation is complete and excess nitrous acid is present.

The diazonium salt solution is now ready for use. It should be kept cold.

The diazo coupling reaction

5. Dissolve a few crystals (or drops) of your chosen coupling agent in 2 cm^3 of dilute sodium hydroxide solution. Cool this solution to 5 °C. Add 2 cm^3 of cold diazonium salt solution drop by drop and stir. After noting your results, dispose of the products down the sink with lots of water.

Looking at your results

Draw out the structures of the dyes you have made and identify the chromophore in each. Note the colour of each dye. Highlight parts of the molecules which are the same and those which are different. How did the nature of R' and Z affect the colour of the dye?

Compare your results with a group who have used a different diazonium salt in their coupling reactions. How did the nature of R affect the colours of the dyes produced?

Given time and chemicals, what other compounds would you choose to make? What colours would you expect them to be?

QUESTIONS

a Write out equations for the formation of the dyes you have made.

b Why is it essential to keep the diazonium salt solution below 5 °C?

c When phenol dissolves in sodium hydroxide solution, sodium phenoxide is formed. Write down its formula. Suggest why this is used in the coupling reaction rather than phenol itself.

CD7.1

Dyeing with a direct dye and a reactive dye

In this activity you will dye cotton cloth with a fibre-reactive dye and with a direct dye, and then compare the fastness to washing.

Requirements

- samples of untreated white cotton cloth (about 5 g each) (2)
- protective gloves
- 400 cm^3 beakers (2)
- Durazol Red 2B solution (a direct dye) (250 cm^3)*
- Procion Red MX-5B solution (a reactive dye) (200 cm^3)*
- sodium chloride (13 g)
- sodium carbonate (0.5 g)
- stirring rods
- tongs
- soap powder
- strip chromatography paper
- beaker to use as chromatography tank
- Bunsen burner, tripod and gauze

* See instructions for preparation in the Teacher's and Technician's Guide

Durazol Red 2B

Procion Red MX-5B

sodium carbonate

CARE Eye protection must be worn.

CARE Avoid all skin contact with the dyes. Gloves must be worn.

What you do

You are given instructions for dyeing cotton cloth with two different dyes, a fibre-reactive dye and a direct dye.

Dye samples of white cotton with the two dyes and then compare their fastness to washing. While you are dyeing the cotton samples, you can investigate the hydrolysis of the reactive dye in the dyebath using chromatography.

Dyeing cotton with a direct dye

1 First make up the dyebath. Put 250 cm^3 of Durazol Red 2B solution (**CARE** Irritant) into a 400 cm^3 beaker and add 1 g of sodium chloride. Heat until boiling. Immerse the cotton cloth in the dyebath and continue heating for 10 minutes with occasional stirring. Remove the cloth and rinse it thoroughly with water.

Dyeing cotton with a reactive dye

2 Put 200 cm^3 of Procion Red MX-5B solution (**CARE** Irritant) into a 400 cm^3 beaker. Immerse the cotton cloth and then add 12 g of sodium chloride in small amounts over 5 minutes. Leave the mixture to stand for 10 minutes, stirring from time to time. Then add 0.5 g of sodium carbonate and stir until dissolved.

3 Continue the dyeing with occasional stirring for a further 30 minutes. Remove the cloth and rinse it well with water. Finally, wash the cloth thoroughly in hot soap solution.

How much dye is hydrolysed?

One problem with fibre-reactive dyes is that they are hydrolysed in solution. The dye breaks down and the *dichlorotriazinyl* group, which attaches the dye to the fibre, is lost.

You can investigate the extent of the hydrolysis reaction using chromatography. Chromatography paper reacts with the dye in a similar way to cotton. Both are made of cellulose.

4 Put a spot of the Procion Red MX-5B dye solution (containing sodium chloride) onto a strip of chromatography paper. Leave for 10 minutes and then add a drop of concentrated sodium carbonate solution to the spot. Stand the paper in a 1 cm depth of water in a beaker, making sure the water level is *below* the spot. Allow the water to rise up the paper. The dye which has reacted with the paper will not move. Any hydrolysed dye will move up the paper with the water.

Fastness testing

5 Devise a procedure for testing your dyed samples for fastness to washing. Remember that when clothes are washed, it is important that the colours do not fade, and also that colours are not transferred from one garment to another. The instructions on a packet of washing powder will give you an idea of the conditions suitable for testing fastness to washing.

Results

6 Write a short report summarising your findings. It should include the following points:

- How did the appearance of the two samples of dyed cloth compare?
- What are the advantages and disadvantages of each dyeing process?
- How did fastness to washing of the two dyes compare?

Be prepared to make an oral presentation of your results. Compare your findings with those of other groups.

CD7.2

Different dyes for different fibres

This activity demonstrates how a knowledge of the structure of dyes and fibres enables chemists to dye successfully a wide variety of fabrics.

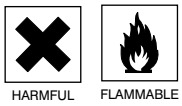
Requirements

- protective gloves
- 400 cm^3 beaker
- stirring rod
- tongs
- dye mixture (10 cm^3)*
- small samples (about 20 cm^2) of white cotton, polyester and nylon
- apparatus for paper chromatography
- chromatography solvent (95% butanol:5% water)

CARE Use the butanol solvent in a fume cupboard or well-ventilated area. Keep away from naked flames.

* See instructions for preparation in the Teacher's and Technician's Guide

butanol



dye mixture

CARE Eye protection must be worn.

CARE Avoid skin contact with the dye solution. Gloves must be worn.

What you do

You are provided with a mixture of three dyes. First, you will use the dye mixture to dye three types of fabric as described below. Different fibres have different structures and bind dyes to different extents.

You can then investigate the composition of the dye mixture using chromatography.

Finally, you will use your observations, together with your knowledge of fibres and how dyes bind to fibres, to assign structures to each of the dyes in the mixture.

Dyeing different fabrics with the dye mixture

1 Dilute 10 cm^3 of the dye mixture (**CARE** Irritant) to 100 cm^3 with water. Heat the solution to boiling in a 400 cm^3 beaker. Add small strips of white cotton, polyester and nylon. Avoid using fabrics with a mixed composition.

2 Allow the pieces of fabrics to boil gently in the dye solution for 10–15 minutes. Remove the samples with tongs, rinse well with cold water and allow to dry. Note the colour of the various fabrics.

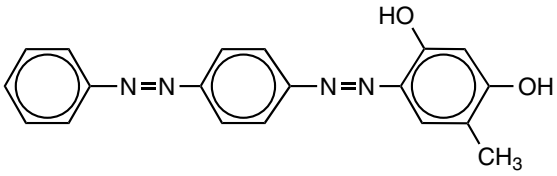
What's in the dye mixture?

3 Investigate the composition of the dye mixture using paper chromatography, with a 95% butanol : 5% water mixture as the solvent (**CARE** Flammable and harmful).

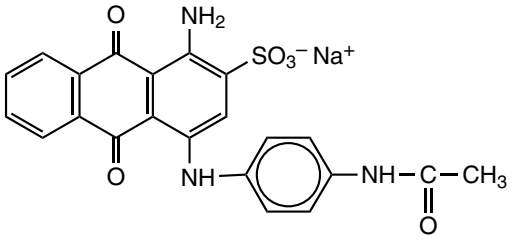
Which dye is which?

The three dyes in the mixture have the following structures, X, Y and Z.

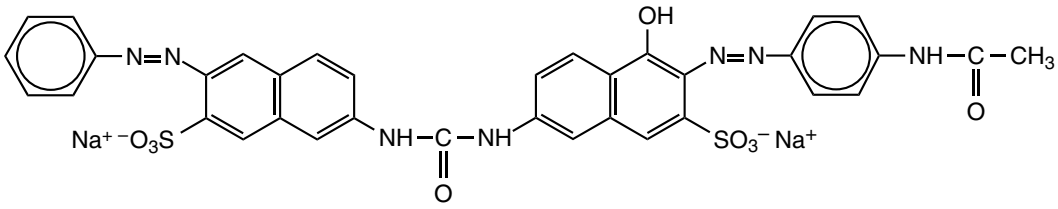
dye X



dye Y



dye Z



4 Use your knowledge of how dyes bind to fibres, together with your observations, to assign structures X, Y and Z to each of the three dyes in the mixture. Explain your reasoning.

Remember that paper is a cellulose polymer made up of glucose units, like cotton. You made need to look back to **Designer Polymers** for the structure of nylon and polyester fibres. Polyesters are relatively non-polar. Water does not penetrate the fibres well and the fabric is best dyed with small, relatively non-polar molecules. The main attractive forces between the dye molecules and the polyester fibres are instantaneous dipole–induced dipole forces. Nylon too has non-polar sections in its fibres, but also has $-NH_3^+$ groups at the end of the chains in acid solution.

What's the use?

5 Suggest ways in which a textile manufacturer might use a dye mixture of this type.

CD9

Check your notes on *Colour by Design*

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.

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 absorption of ultraviolet light and visible light in terms of transitions between electronic energy levels.
- The use of ultraviolet (u.v.) and visible spectroscopy to help identify unsaturated organic molecules.
- Colour changes associated with the following types of chemical changes: acid–base (indicators), ligand exchange, redox, precipitation and polymorphism (different crystal structures).
- The relationship between the properties of pigments (colour shade, colour intensity, fastness) to relevant properties (**Storyline CD2** and **CD3**).
- The general principles of gas-liquid chromatography (g.l.c.).
- The techniques used to identify the materials used in a painting, including the use of g.l.c., atomic emission spectroscopy, and visible spectroscopy (reflection and transmission) (**Storyline CD3** and **CD4**; **Activities CD4.1–4.5**).
- The nature of fats and oils as mixed esters of propane-1,2,3-triol with varying degrees of unsaturation.
- An outline of the process of oxidative cross-linking by which unsaturated oils harden; the relationship of this process to their use as media in oil-based paints.
- What arenes and arene derivatives (aromatic compounds) are.
- The structure of benzene.
- How the characteristic properties of aromatic compounds arise from the delocalisation of electrons.
- The following electrophilic substitution reactions of arenes: halogenation of the ring, nitration, sulphonation, Friedel-Crafts alkylation and Friedel-Crafts acylation.
- The formation of azo dyes by coupling reactions involving diazonium compounds.
- The structure of a dye molecule in terms of its various components: chromophore, groups which modify the chromophore, groups which made the dye more soluble in water and groups which attach the dye to the fibre (**Storyline CD5–CD7**).
- Ways in which dyes attach themselves to fabrics: weak intermolecular forces, hydrogen bonds, ionic attractions and covalent bonding (**Storyline CD7**; **Activity CD7.2**).
- The relationship between the colour of a dye and the presence of a chromophore, and groups that modify the chromophore, in the dye molecule.
- The relationship between colour in materials and transitions between electronic energy levels.

01.1

What is the relationship between a solvent and the substances that dissolve in it?

***In this activity you investigate the solubilities of four substances in three different solvents. You can draw some general conclusions about solubility from the data you collect, and explain your observations in terms of chemical ideas you have learned during the course. You may need to revise ideas about chemical bonding* (Chemical Ideas 3.1 *and* 5.1), *intermolecular forces* (Chemical Ideas 5.3, 5.4 *and* 5.6), *and the enthalpy and entropy changes during solution* (Chemical Ideas 4.5).**

Requirements

- the following solids, in powdered form in stoppered specimen tubes (about 2 g of each):
  - anhydrous sodium chloride
  - anhydrous calcium chloride
  - glucose (or sucrose)
- grated candle wax (2 g)
- test-tubes (3) and rack
- hexane (12 cm^3)
- propanone (12 cm^3)
- distilled water (12 cm^3)

CARE Hexane and propanone are highly flammable liquids. Keep bottles stoppered when not in use and well away from naked flames. Avoid skin contact and do not breathe the vapours. Return residues to the correct residues bottle. Do not pour them down the sink.

calcium chloride

IRRITANT

hexane

HARMFUL

HIGHLY FLAMMABLE

propanone

HIGHLY FLAMMABLE

CARE Eye protection must be worn.

WEAR EYE PROTECTION

What you do

1 Test the solubilities of the solids in the different solvents using the method described in **Activity M1.3** of **From Minerals to Elements**. (**CARE** Hexane and propanone are highly flammable. Extinguish all flames before using these liquids. Avoid skin contact and do not breathe vapours. Return residues to the correct residue bottle. Do not pour them down the sink.)

It may be best for each pair of students to investigate the solubility of one solid in the range of solvents, and then join with other pairs to produce a full table of results.

2 Use the information contained in your results table to work through the points which follow.

Looking at your results

a For each of the seven substances used (four solids and three solvents), decide whether its bonding is ionic or covalent. If it is covalent, are the molecules polar or non-polar?

b What general pattern of solubility do you observe from your results?

To interpret your results fully you should read about energy changes in solution in **Chemical Ideas 4.5**. Entropy changes usually favour solution but the process is often prevented by a large endothermic enthalpy change of solution.

We can find out whether dissolving is likely to be accompanied by a large endothermic enthalpy change by considering the interactions between the particles in the separate solids and liquids, and between the particles in the solutions which might form from them. For example, if the attractive forces between particles in the pure solid and in the pure solvent are stronger than those between particles in solution, the enthalpy change of solution is likely to be endothermic.

c Fill in Table 1, and use it to explain why solutions form or do not form in each case.

Solid	Principal interactions in solid	Solvent	Principal interactions in solvent	Principal interactions in solution	Enthalpy change which would accompany the formation of a solution as a result of these changes in interactions	Is the solid likely to dissolve?
NaCl		hexane				
		propanone				
		water				
$CaCl_2$		hexane				
		propanone				
		water				
glucose		hexane				
		propanone				
		water				
wax		hexane				
		propanone				
		water				

Table 1 Changes in interactions between particles when a solid dissolves

O1.2

What changes occur when an ionic solid dissolves?

This activity looks in more detail at the changes which occur when ionic solids dissolve. It provides evidence to support and test the explanations you put forward in Table 1 in* Activity O1.1. *It may be best to share the work so that each student or pair of students chooses one solid to study in both parts of the activity.

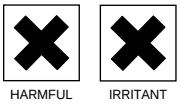
Requirements

- the following solids, in powdered form in stoppered specimen tubes:
  – anhydrous sodium chloride (12 g)
  – anhydrous calcium chloride (23 g)
  – anhydrous iron(III) chloride (33 g)
- distilled water (300 cm^3)
- polystyrene cups (or insulated beakers)
- 0–110 °C thermometer
- 50 cm^3 measuring cylinder
- burettes (2)
- weighing bottles with stoppers
- rubber bungs to fit burettes
- small funnel
- access to balance

calcium chloride

IRRITANT

iron(III) chloride



HARMFUL IRRITANT

CARE Eye protection must be worn.

WEAR EYE PROTECTION

What you do

Note Calcium chloride and iron(III) chloride each take in water from the air. It is important to use *fresh anhydrous* samples and to work quickly.

Part 1: Enthalpy changes

1 Place 50 cm^3 of distilled water in a polystyrene cup and record its temperature.

2 Weigh out enough solid to produce a solution of concentration 2.0 mol dm^{-3}.

3 Add the solid to the water. *Carefully* stir the mixture with the thermometer and record the highest or lowest temperature of the solution.

4 Calculate the temperature change and from it the molar enthalpy change of solution ($\Delta H_{solution}$) (i.e. the enthalpy change when 1 mole of solid dissolves to form a 2.0 mol dm^{-3} solution).

5 Repeat the procedure in steps **1**–**4** for the other two solids.

6 Draw up a table to show your results.

Part 2: Volume changes

This part of the activity uses a burette to make accurate measurements of the volume changes which accompany the formation of a solution. Burettes contain an ungraduated section and you have to be careful when filling the burette to make sure it contains only 50 cm^3 of water. One way of doing this is to add exactly 50 cm^3 of water from another burette (or a pipette) to your empty burette.

7 Weigh out enough solid to make 50 cm^3 of a 2.0 mol dm^{-3} solution.

8 Place 50 cm^3 of water into the burette, then pour in a little of the solid through a small funnel. Stopper the burette and invert it several times to mix the contents. Continue adding the solid until it has all dissolved.

9 Record the volume of the solution.

10 Repeat the procedure in steps **7**–**9** for the other two solids.

11 Calculate the volume of the solid you added in each case, using its mass and the density given below.

Solid	Density/g cm^{-3}
sodium chloride	2.2
calcium chloride	2.5
iron(III) chloride	2.8

12 Use the relationship

volume change =
(volume of solution) – (volume of solid + volume of water)

to work out in each case the change in volume when the solid dissolves.

13 Draw up a table to show your results.

Interpreting your results

You may wish to revise ideas about the hydration of ions in **Chemical Ideas 3.2** and **5.1** to help you with this part of the activity.

a Interpret the enthalpy changes measured in Part 1 in terms of the processes that occur when the solids dissolve and the interactions between the chemical particles present.

b Use these ideas to explain the volume changes you noted in Part 2 of the activity.

01.3

What factors affect the enthalpy change of formation of an ionic compound?

In this activity you will see how the formation of an ionic compound from its constituent elements can be imagined to take place in several stages, each with its own enthalpy change. The values of these enthalpy changes determine the overall value for the enthalpy change of formation of the compound.

Part 1: Constructing an enthalpy cycle

The standard enthalpy change of formation of sodium chloride, $\Delta H_f^\ominus(NaCl(s))$, is the enthalpy change for the reaction:

$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$ $\quad \Delta H_f^\ominus(NaCl(s)) =$ standard enthalpy change of formation of sodium chloride

You can imagine the stages involved as:
(1) turning the elements Na(s) and $Cl_2(g)$ into gaseous atoms
(2) turning the atoms into gaseous ions
(3) bringing the gaseous ions together to form NaCl(s)

The following equations describe the stages:
(a) $Na(s) \rightarrow Na(g)$
(b) $Na(g) \rightarrow Na^+(g) + e^-$
(c) $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$
(d) $Cl(g) + e^- \rightarrow Cl^-(g)$
(e) $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$

1 Draw up a table and match the equations (a) to (e) with the stages (1) to (3) above.

2 Each of the equations (a) to (e) defines a standard enthalpy change. Match the enthalpy changes (i) to (v) below with the equations (a) to (e).

(i)	lattice enthalpy of sodium chloride	$\Delta H_{LE}^\ominus(NaCl(s))$
(ii)	first electron affinity of chlorine	$\Delta H_{EA}^\ominus(Cl(g))$
(iii)	standard enthalpy change of atomisation of sodium	$\Delta H_{at}^\ominus(Na(s))$
(iv)	standard enthalpy change of atomisation of chlorine	$\Delta H_{at}^\ominus(\frac{1}{2}Cl_2(g))$
(v)	first ionisation enthalpy of sodium	$\Delta H_i^\ominus(1)\ (Na(g))$

3 Draw out the enthalpy cycle showing how you get from the elements in their standard states, Na(s) and $\frac{1}{2}Cl_2(g)$, to the compound, NaCl(s), using the stages defined by the equations (a) to (e). Label each stage with the appropriate symbol taken from (i) to (v). This type of enthalpy cycle for a simple ionic compound is known as a **Born-Haber** cycle.

4 Apply Hess's Law to the cycle and obtain an equation that shows how $\Delta H_f^\ominus(NaCl(s))$ depends on the other enthalpy changes.

5 Set up a spreadsheet that will calculate $\Delta H_f^\ominus$ for any Group 1 halide. The only data input required will be the values for the enthalpy changes (i) to (v).

Part 2: Using the cycle

6 Use bar charts, from your spreadsheet, to explore how $\Delta H_f^\ominus$ depends on $\Delta H_{LE}^\ominus$ and $\Delta H_i^\ominus(1)$ for the series of compounds:

i NaF, NaCl, NaBr, NaI
ii LiCl, NaCl, KCl, RbCl

Comment on any patterns you see.

QUESTION

How would you need to adapt your enthalpy cycle and spreadsheet to cope with the halides of Group 2 elements?

03.1 The enthalpy change of vaporisation of water

The first part of this activity is optional. It introduces you to some practical techniques which you have not previously encountered in the course, and allows you to measure a value for the enthalpy change of vaporisation (ΔH_{vap}) of water. You can then compare this with values for some other liquids and use the ideas you have learned in* Chemical Ideas 4.4 *to interpret the results.

Part 1: Measuring the enthalpy change of vaporisation of water (Optional extension)

Requirements

- 12 V d.c. supply
- joulemeter
- electrical heating coil (see Figure 1)
- apparatus for boiling and condensing water (see Figure 1)
- small beakers or specimen tubes (2)
- access to balance

CARE Eye protection must be worn.

What you do

1 Assemble the apparatus shown in Figure 1, for boiling and condensing water. Use water close to boiling in the side-arm boiling tube.

2 Position one small beaker as shown in the diagram; have a second weighed beaker ready.

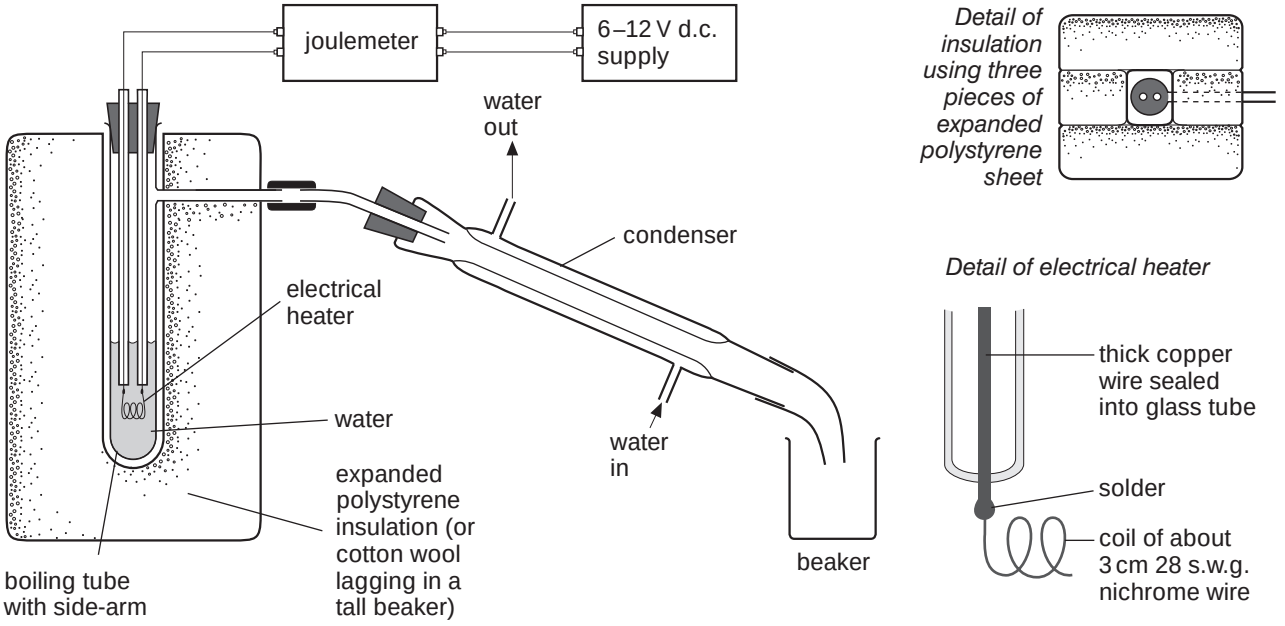


Figure 1 Apparatus for measuring the enthalpy change of vaporisation of water

3 Switch on the power. Allow the water to warm up and then boil for a few minutes until it drips at a slow steady rate from the condenser into the unweighed small beaker. Then change over the beakers and simultaneously reset the joulemeter.

4 Allow about 3 cm^3 of water to distil over, then exchange the beakers once more, reading the joulemeter at the same instant.

5 Record the mass of beaker plus water and calculate the mass of water collected.

Part 2: Looking at your results

*You should do this part of the activity even if you have not done the practical in Part 1. The questions which follow should encourage you to apply what you have learned in **Chemical Ideas 4.4**. Make sure you have read these ideas before you attempt the questions.*

a Calculate a value for ΔH_{vap} for water in kJ mol^{-1}. (In a typical student's experiment, 8100 J were needed to distil 2.95 g of water.)

b Explain why the boiling tube is surrounded with expanded polystyrene but the condenser is left uncovered.

c Before any water was collected, the water was allowed to boil for several minutes until drops fell steadily from the condenser. Explain why this helps you achieve greater accuracy in your estimate of ΔH_{vap}.

Table 1 lists values of ΔH_{vap} and boiling point (T_b) for water and four organic compounds.

Liquid	Formula	ΔH_{vap}/kJ mol^{-1}	T_b/K
trichloromethane	$CHCl_3$	+29.3	335
hexane	C_6H_{14}	+28.8	342
cyclohexane	C_6H_{12}	+30.1	354
methylbenzene	C_7H_8	+33.4	384
water	H_2O	+40.6	373

Table 1 Enthalpy changes of vaporisation (ΔH_{vap}) and boiling points (T_b) for some compounds

d i Water has a high ΔH_{vap} value compared with the other substances in Table 1. Use your knowledge of intermolecular forces to explain this observation.

ii Ethanol also has an unusually high ΔH_{vap} value of +38.5 kJ mol^{-1}. Explain how the changes which occur during boiling are similar for ethanol and water.

e All the ΔH_{vap} values are highly endothermic. Nevertheless, the compounds are volatile and can easily be boiled. What other change which favours the process accompanies vaporisation?

f i At the boiling point, a liquid and its vapour are in equilibrium. What can you say about the total entropy change for a system which is at equilibrium?

ii What is the relationship between the entropy change on vaporisation of a liquid (ΔS_{vap}) and the entropy change in the surroundings (ΔS_{surr}) at the boiling point?

iii ΔS_{surr} during an endothermic change can be calculated from the thermal energy supplied and the temperature at which the change occurs. For boiling, the relationship is:

$$\Delta S_{surr} = \frac{-\Delta H_{vap}}{T_b}$$

Use this relationship to calculate ΔS_{surr} values for the five compounds in Table 1.

g i Use your answers for **f ii** and **f iii** to calculate ΔS_{vap} values for the five compounds in Table 1.

ii What general observation can you make about the values of ΔS_{vap} for the four organic compounds in Table 1?

iii Explain this observation in terms of the molecular-kinetic model which chemists use to describe the structures of liquids and vapours.

iv How does the value of ΔS_{vap} for water compare with the value you found for the four organic liquids? Explain why there is a difference.

h i Convert the values for ΔH_{vap} in Table 1 into kJ kg^{-1}.

ii These figures should show you that, for the transport of a given mass of vapour through the atmosphere, water carries much more energy with it than the other substances. Explain why this is important for the climate of the Earth.

03.2

What crystals form when a solution is cooled?

Freezing and crystallisation cause density changes in the oceans and are among the factors that drive ocean currents. This activity uses copper(II) sulphate, which is easy to distinguish from ice crystals, to investigate the effect of cooling solutions containing different concentrations of an ionic compound.

The questions, which help you to interpret your observations, also provide an opportunity for you to reinforce what you have learned in* Chemical Ideas *4.4 about entropy changes and their relationship to enthalpy changes and temperature.

Requirements

- saturated copper(II) sulphate solution (4 cm^3)
- 250 cm^3 beaker
- test-tubes (2) and rack
- crushed ice
- table salt
- –10 °C–110 °C thermometer

copper(II) sulphate

HARMFUL

CARE Eye protection must be worn.

WEAR EYE PROTECTION

What you do

1 Make an ice–salt freezing bath by mixing crushed ice and table salt in a beaker.

2 Place about 3 cm^3 of saturated copper(II) sulphate solution in one test-tube. Add 1 cm^3 of saturated copper(II) sulphate solution to 2 cm^3 of water in the other test-tube.

3 Place the test-tubes into the freezing bath and allow the solutions to cool. Make a note of the temperature at which crystals form in each solution, the appearance of the crystals, and whether they float or sink.

4 Before you throw away the contents of the freezing bath, make a note of its temperature and appearance.

What it means

a When a solution of copper(II) sulphate cools, what determines whether it is water or copper(II) sulphate that crystallises out first?

b Describe how you think the density of a copper(II) sulphate solution changes when:
i copper(II) sulphate crystals form
ii ice crystals form.

c The salt concentration in sea water is typically about 0.5 mol dm^{-3}. How might ocean currents be affected if the sea were saturated with salt?

d The enthalpy change when water freezes to form ice is –6010 J mol^{-1}. What will be the gain in entropy of the surroundings when water freezes at 273 K?

e At 273 K the entropy of ice is lower than the entropy of water by 22.0 J K^{-1} mol^{-1}. Explain why the entropy of ice is lower.

f Comment on the total entropy change of the system and surroundings that accompanies the freezing of water at 273 K.

g The enthalpy change (ΔH) when pure water freezes to produce ice is the same as the enthalpy change when copper(II) sulphate solution freezes to produce ice. However, ice crystals do not form from copper(II) sulphate solution until the temperature has fallen below 273 K. This is because the entropy changes (ΔS_{sys}) are different for the two processes.

i For which process will the entropy change (ΔS_{sys}) be greater:
pure water → ice at its freezing point; or
copper(II) sulphate solution → ice at its freezing point?
Explain your answer.

ii At the freezing point, ice is in equilibrium with the water or solution which is freezing. Therefore ΔS_{total} must be zero. You have made decisions about ΔS_{sys} in **g i**. How must ΔS_{surr} compare for the two processes:
pure water → ice at its freezing point; and
copper(II) sulphate solution → ice at its freezing point?

iii The entropy change in the surroundings (ΔS_{surr}) is related to ΔH and the temperature at which freezing occurs. Use this relationship to explain why ice forms from copper(II) sulphate solution at a temperature below 273 K.
The same idea explains why it is possible to have water, ice and salt present together at temperatures well below 273 K. So you can melt ice on roads in winter, and make it run off, by adding salt. You can also make freezing baths like the one you used in this activity.

04.1 Finding out more about weak acids

***You can compare some of the properties of weak and strong acids by using ethanoic acid as a typical weak acid and hydrochloric acid as a typical strong acid. The measurements you make can be interpreted in terms of the theory in* Chemical Ideas 8.2.**

By the end of the activity you should have seen that pH is less sensitive to changes in weak acid concentration than strong acid concentration. You should then appreciate one of the reasons why the thousandfold change in atmospheric carbon dioxide concentration that has occurred during the Earth's history has not caused a major change in the pH of the oceans.

Requirements

- pH meter
- 100 cm^3 beaker
- solutions of hydrochloric acid of the following concentrations (about 50 cm^3 of each solution):
  - 0.1 mol dm^{-3}
  - 0.03 mol dm^{-3}
  - 0.01 mol dm^{-3}
  - 0.003 mol dm^{-3}
  - 0.001 mol dm^{-3}
- solutions of ethanoic acid of the same concentrations as above (about 50 cm^3 of each solution)

CARE Eye protection must be worn.

What you do

1 Pour sufficient 0.001 mol dm^{-3} hydrochloric acid into a beaker to allow you to measure the pH. Record the pH and return the solution to the stock bottle.

2 Repeat the measurements with the other hydrochloric acid solutions. If you work from the lowest to the highest concentration you can use the same beaker, and there is no need to rinse it out or clean the glass electrode between readings.

3 Now repeat steps **1** and **2** using the ethanoic acid solutions. Before you start, make sure the glass electrode is rinsed with distilled water to remove all traces of hydrochloric acid.

4 Present all your results in the form of a table.

Discussion of results

a **i** Explain what you understand by the term pH.
ii Explain how changes in pH and changes in $[H^+(aq)]$ are related.

b From your results, what appears to be the pH change associated with:
i a 10-fold change in the concentration of hydrochloric acid?
ii a 100-fold change in the concentration of ethanoic acid?

c **i** Explain what you understand by the term *strong acid*. How is this different from a *concentrated acid*?
ii Explain why you would expect a 10-fold change in the concentration of a strong acid to lead to a 10-fold change in $[H^+(aq)]$.
iii How does your answer to **b i** compare with the behaviour you would expect of a strong acid?

d **i** Explain what you understand by the term *weak acid*.
ii Write an expression for the acidity constant (K_a) of ethanoic acid. (You can abbreviate the formula to HA for convenience.)
iii It is reasonably accurate to regard $[H^+(aq)]$ and $[A^-(aq)]$ as being equal in the solutions of ethanoic acid used in this activity. Explain why we can do this.
iv Another reasonably accurate assumption is to regard [HA(aq)] as equal to the amount of acid used to make 1 dm^3 of each solution. For example, we can say [HA] = 0.1 mol dm^{-3} in ethanoic acid solution of concentration 0.1 mol dm^{-3}. Explain why this is an accurate assumption.
v Rewrite K_a for ethanoic acid solutions of concentrations 0.1 mol dm^{-3} and 0.001 mol dm^{-3}, using the assumptions discussed in **d iii** and **iv**. You should be left with expressions for K_a which involve only $[H^+(aq)]$ and numbers.
vi How does the value for $[H^+(aq)]$ change when a 0.1 mol dm^{-3} solution of ethanoic acid is diluted by a factor of 100, to 0.001 mol dm^{-3}?
vii You have just worked out how you would expect $[H^+(aq)]$ and [HA(aq)] to be related for ethanoic acid – an example of a weak acid. How does the observation you made in **b ii** compare with this expected behaviour?

04.2 Investigating some buffer solutions

***In this activity you make pH measurements of some buffer solutions and see what happens when you add water, acid and alkali to them. You then compare their behaviour to a solution of similar pH that is not a buffer. Interpreting the results should reinforce the ideas you learned about in* Chemical Ideas 8.3.**

Requirements

- 0.5 mol dm^{-3} solutions of the following:
  - ethanoic acid (75 cm^3)
  - potassium (or sodium) ethanoate (75 cm^3)
  - methanoic acid (25 cm^3)
  - potassium (or sodium) methanoate (25 cm^3)
  - ammonium chloride (25 cm^3)
  - ammonia solution (25 cm^3)
  - hydrochloric acid (15 cm^3)
  - potassium (or sodium) hydroxide (15 cm^3)
- 25 cm^3 measuring cylinder
- 10 cm^3 measuring cylinder
- distilled-water wash bottle
- 100 cm^3 beakers (7)
- pH meter
- 1 × 10^{-4} mol dm^{-3} nitric(V) acid (50 cm^3)
- glass rod

potassium hydroxide solution

IRRITANT

CARE Eye protection must be worn.

WEAR EYE PROTECTION

What you do

As you work through this activity, fill in your results in Table 1.

1 Make up three buffer solutions by mixing 25 cm^3 portions of the 0.5 mol dm^{-3} solutions in the pairs listed below. (Use 100 cm^3 beakers to hold the buffer solutions and stir each one with a glass rod.)

Buffer A ethanoic acid + potassium ethanoate
Buffer B methanoic acid + potassium methanoate
Buffer C ammonium chloride + ammonia solution

Measure the pH of each buffer using a pH meter. Rinse the glass electrode with distilled water between measurements.

2 Remove 5 cm^3 of Buffer A and add it to 45 cm^3 of distilled water in a fourth beaker. This is **Buffer D**. Record its pH.

a How are the pH values of Buffer A and Buffer D related?

b Does the pH of a buffer depend on the *total* amounts of acid and salt present or on the *ratio* of their amounts? Explain your answer.

3 Make up two more buffers using 0.5 mol dm^{-3} ethanoic acid and 0.5 mol dm^{-3} potassium ethanoate as follows:

Buffer E 10 cm^3 ethanoic acid + 40 cm^3 potassium ethanoate
Buffer F 40 cm^3 ethanoic acid + 10 cm^3 potassium ethanoate

Record the pH values.

c Use Le Chatelier's principle to explain the way the pH values vary among the Buffers A, E and F.

The measurements you have made show that buffers can have pH values spread over a wide range. There are two steps to designing a buffer with a particular pH:

- 'coarse tuning' to select the pH region
- 'fine tuning' to adjust the pH to the actual value required.

You have seen that the pH of a buffer depends on:

- the chemical system chosen
- the proportions of acid and salt used.

d Which of these two factors would you make use of in
i the 'coarse tuning'
ii the 'fine tuning'?

4 Place 50 cm^3 of 1×10^{-4} mol dm^{-3} nitric(V) acid into another beaker. This is **Solution G**; it has a similar pH to the ethanoic acid + potassium ethanoate mixtures, but it is not a buffer solution.

Add 3 cm^3 of 0.5 mol dm^{-3} hydrochloric acid to solutions A, D and G. Record the pH changes.

e Explain the different effects of adding the same amount of hydrochloric acid to these three solutions.

5 Add 3 cm^3 of 0.5 mol dm^{-3} hydrochloric acid or potassium hydroxide to buffers B, C, E and F. You are free to choose which solutions to add to which buffers. Record the pH changes.

f Explain the effects of adding acid or alkali to the buffers.

Solution	System	pH	ΔpH + 3 cm^3 HCl	ΔpH + 3 cm^3 KOH	Was the solution an effective buffer?
A					
B					
C					
D					
E					
F					
G					

Table 1 Results table

05

Check your notes on *The Oceans*

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.

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.

- Factors that determine the relative solubility of a solute in aqueous and non-aqueous solvents.
- The meaning and use of the terms: *enthalpy change of solution*, *lattice enthalpy*, *enthalpy of solvation (hydration)*.
- The solution of an ionic solid in terms of an enthalpy cycle involving enthalpy change of solution, lattice enthalpy and enthalpies of solvation (hydration) of ions.
- The effect of atomic number, charge and hydration on the radii of anions and cations.
- The relationship between ionic size and properties.
- The Born-Haber cycle for simple ionic compounds.
- Entropy as a measure of the number of ways that molecules and their associated energy quanta can be arranged.
- The process of dissolving in terms of energy and entropy factors.
- The tendency of a process to occur in terms of entropy changes in the system (ΔS_{sys}) and surroundings (ΔS_{surr}), and the requirement that the total entropy change (ΔS_{total}) should be positive.
- Calculations of entropy changes using the expression: $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$.
- Calculation of entropy changes for a reaction given entropies of reactants and products.
- Comparison of the following properties of water with those of other liquids, and other hydrides of Group 6 elements, and the relationship of these properties to molecular structure: specific heating capacity, enthalpy change of vaporisation, and density changes on melting.
- The influence of oceans on climate in terms of the characteristic properties of water (**Storyline O3**).
- The meaning and use of the following terms: *strong acid*, *strong base*, *pH*.
- The ionic product of water, K_w.
- Calculation of the pH of solutions of strong acids and strong bases.
- The meaning and use of the following terms: *weak acid*, *acidity constant* K_a, pK_a.
- Calculation of the pH of solutions of weak acids.
- How buffer solutions work, and their applications.
- Calculation of the pH of a buffer solution.
- The meaning and use of the term *solubility product* for simple ionic compounds of formula $X^{n+}Y^{n-}$.
- The use of solubility products to perform calculations concerning dissolving and precipitation processes.
- Acid–base and precipitation processes in the oceans in terms of K_a and K_{sp} (**Storyline O4**).
- The global influence of the processes occurring when carbon dioxide dissolves in water (**Storyline O4**).

MDI.I

Aldehydes and ketones

This activity considers the formation and reactions of aldehydes and ketones.

Requirements

- potassium dichromate(VI) solution, 0.1 mol dm^{-3} (2 cm^3)
- protective gloves
- dilute sulphuric acid, 2 mol dm^{-3} (10 cm^3)
- propan-1-ol (3 drops)
- propan-2-ol (3 drops)
- 2-methylpropan-2-ol (3 drops)
- test-tubes and rack
- propanal (3 drops)
- propanone (3 drops)
- angled glass tubing and rubber bung
- Bunsen burner, tripod and gauze
- 400 cm^3 beaker (for hot water bath)
- Fehling's solution 1 (2 cm^3)
- Fehling's solution 2 (2 cm^3)

CARE Propanal, propanone and the alcohols are highly flammable liquids. Keep bottles stoppered when not in use and well away from naked flames. Avoid skin contact and do not breathe the vapours.

CARE Dichromates(VI) irritate the skin and are suspected carcinogens. Avoid all skin contact. Any spillage should be washed off at once. Wear protective gloves.

Fehling's solution 1
Fehling's solution 2


CORROSIVE


HARMFUL

potassium dichromate(VI) solution


TOXIC

propan-1-ol
propan-2-ol
2-methylpropan-2-ol


HARMFUL


HIGHLY FLAMMABLE

propanal


IRRITANT


HIGHLY FLAMMABLE

propanone


HIGHLY FLAMMABLE

sulphuric acid


CORROSIVE

CARE Eye protection and gloves must be worn.


WEAR EYE PROTECTION


WEAR PROTECTIVE GLOVES

What you do

1 Place about 1 cm depth of 0.1 mol dm^{-3} potassium dichromate(VI) solution (**CARE** Toxic. Avoid skin contact. Wear gloves) in a test-tube. Add 2 mol dm^{-3} sulphuric acid (**CARE** Corrosive) until the tube is half full. Then divide this mixture as equally as possible between five test-tubes.

You are going to investigate the effect of the oxidising mixture on various oxygen-containing compounds starting with propan-1-ol, propan-2-ol and 2-methylpropan-2-ol.

2 Add 3 drops of one of the alcohols to the oxidising mixture in one of the tubes. Be careful not to add too much alcohol. (**CARE** Alcohols are highly flammable. Keep the bottle well away from naked flames.)

Carefully **warm** the contents of the tube until they just begin to boil. (**CARE** Do not continue to boil the liquid in case alcohol vapour catches fire.)

3 Label the tube and leave it to stand. Repeat the procedure in step **2** with each of the other two alcohols.

4 Make a note of any changes of appearance of the mixtures in the tubes. Work out what has happened in each case, and present your results in the form of a table showing the structural formulae of the alcohols and any products which are formed.

5 Where reaction has occurred, distil out a few drops of liquid from each tube using the apparatus shown (Figure 1).

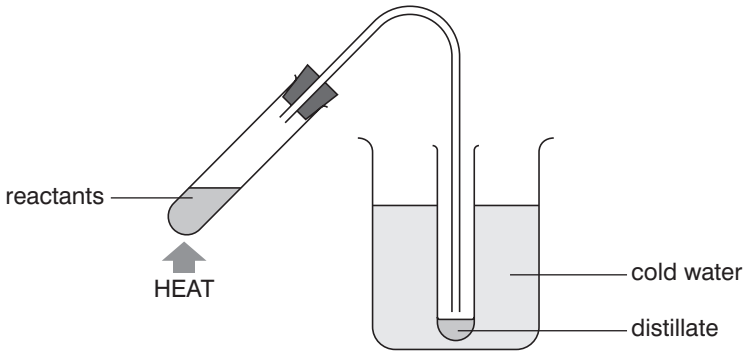


Figure 1 Distilling off the product of oxidation

6 The products which you have distilled over should be propanal and propanone (**CARE** Highly flammable liquids).

Use these liquids, or the liquids from stock bottles of propanal and propanone, and repeat steps **2** and **3** with the two liquids separately.

7 Prepare a hot water bath. A suitable arrangement is a 400 cm^3 beaker half full of water on a tripod and gauze over a Bunsen flame. Transfer about 1 cm^3 of one of the distillates (or reagents from the stock bottle) to a test-tube. Add about 1 cm^3 of Fehling's solution 1 followed by 1 cm^3 of Fehling's solution 2. (**CARE** Fehling's solution 2 contains sodium hydroxide and is corrosive.) Place the test-tube in the hot water bath and observe any colour changes.

Now repeat the experiment with the second liquid.

QUESTIONS

a Which of the alcohols, propan-1-ol, propan-2-ol and 2-methylpropan-2-ol reacted readily with potassium dichromate(VI) solution?

b Account for the change of colour of the mixtures, when one occurs, in the reactions above.

c Write down the full structural formulae of the organic products.

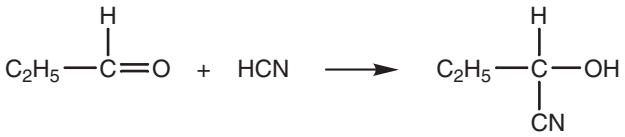
d One of the compounds formed from the reactions above reacts further with potassium dichromate(VI) solution. Write down the structural formulae of this compound and the organic product of this further reaction.

e The red precipitate formed on reaction with Fehling's solution is Cu_2O (the reagent contains $Cu^{2+}(aq)$ ions).

- **i** Suggest what has happened to the organic reagent in the tube when reactions have occurred.
- **ii** Compare this with the process that occurs with the organic reagent and potassium dichromate(VI) solution.

f Propanal and propanone can be reduced to alcohols using the reagent sodium tetrahydridoborate(III), $NaBH_4$. Give the names and structural formulae of the alcohols that will be produced.

g Propanal reacts with hydrogen cyanide, as shown in the equation below:



Write a corresponding equation for the reaction of propanone with hydrogen cyanide.

MDI.2

BAC determination using gas–liquid chromatography

By carrying out this activity you will learn more about the use of g.l.c. for measuring blood-alcohol concentrations. The technique can easily be adapted, and is used to analyse many other kinds of mixture. This activity illustrates ideas about g.l.c. which you learned in* Colour by Design*. You may need to refer to* Chemical Ideas 7.6 *before you begin.

Introduction

A sample which is a mixture of several similar compounds will produce a g.l.c. trace showing separate peaks for each compound. In general, for compounds of the same chemical type, more volatile compounds have shorter g.l.c. retention times.

What you do

Use the following information to investigate how g.l.c. can be used to estimate blood-alcohol concentration (BAC).

1 The chromatogram illustrated in Figure 1 was produced by a mixture of the first five straight-chain primary alcohols.

a Measure the retention times for the five peaks. Record these in a table, together with the name and formula of the alcohol responsible for each peak.

b Estimate a retention time for hexan-1-ol.

2 When blood is analysed for its alcohol content, an exactly measured sample is diluted with water and a standard amount of propan-1-ol is added. A measured sample of this mixture is then analysed by g.l.c.

The gas chromatogram consists of two peaks, corresponding to ethanol and propan-1-ol. The area of each peak is proportional to the amount of compound in the sample, but the instrument's sensitivity may vary from run to run. Using a propan-1-ol standard overcomes this error – the detector will give a high reading for all propan-1-ol peaks if its sensitivity is high, or a low reading for all peaks if the sensitivity is low. In either case, the *ratio* of the ethanol and propan-1-ol peak areas will be the same. It is this ratio which is used to calculate the BAC. For fairness, at least two determinations are made, and the equipment is calibrated periodically using an ethanol solution of known concentration.

Commercial instruments calculate peak areas electronically. However, it is possible to regard a peak as a triangle. The area is then the height of the triangle multiplied by half the length of the base.

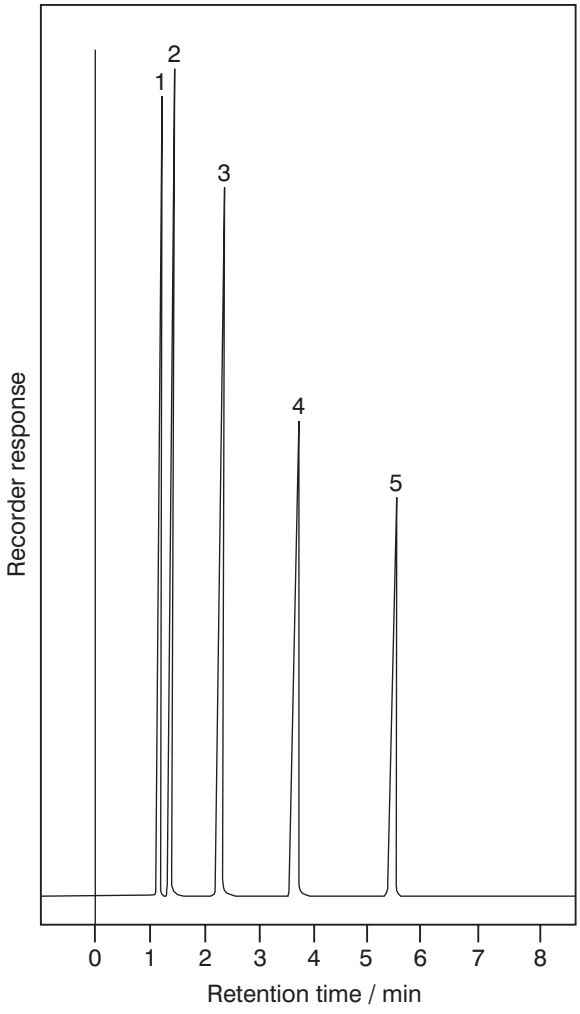


Figure 1 Chromatogram of a mixture of the first five straight-chain primary alcohols: 1, methanol; 2, ethanol; 3, propan-1-ol; 4, butan-1-ol; 5, pentan-1-ol.

Figure 2 shows g.l.c. traces for three blood samples. Trace I corresponds to a BAC of 80.

Note: In practice the peaks are much narrower, as in Figure 1, and the areas under the peaks are found using special computer programs built into the recorders attached to the gas chromatograph. Figure 2 is drawn to enable you to calculate the areas yourself.

Peak area is height times half-width of the triangle obtained by extrapolating the lines of the peak.

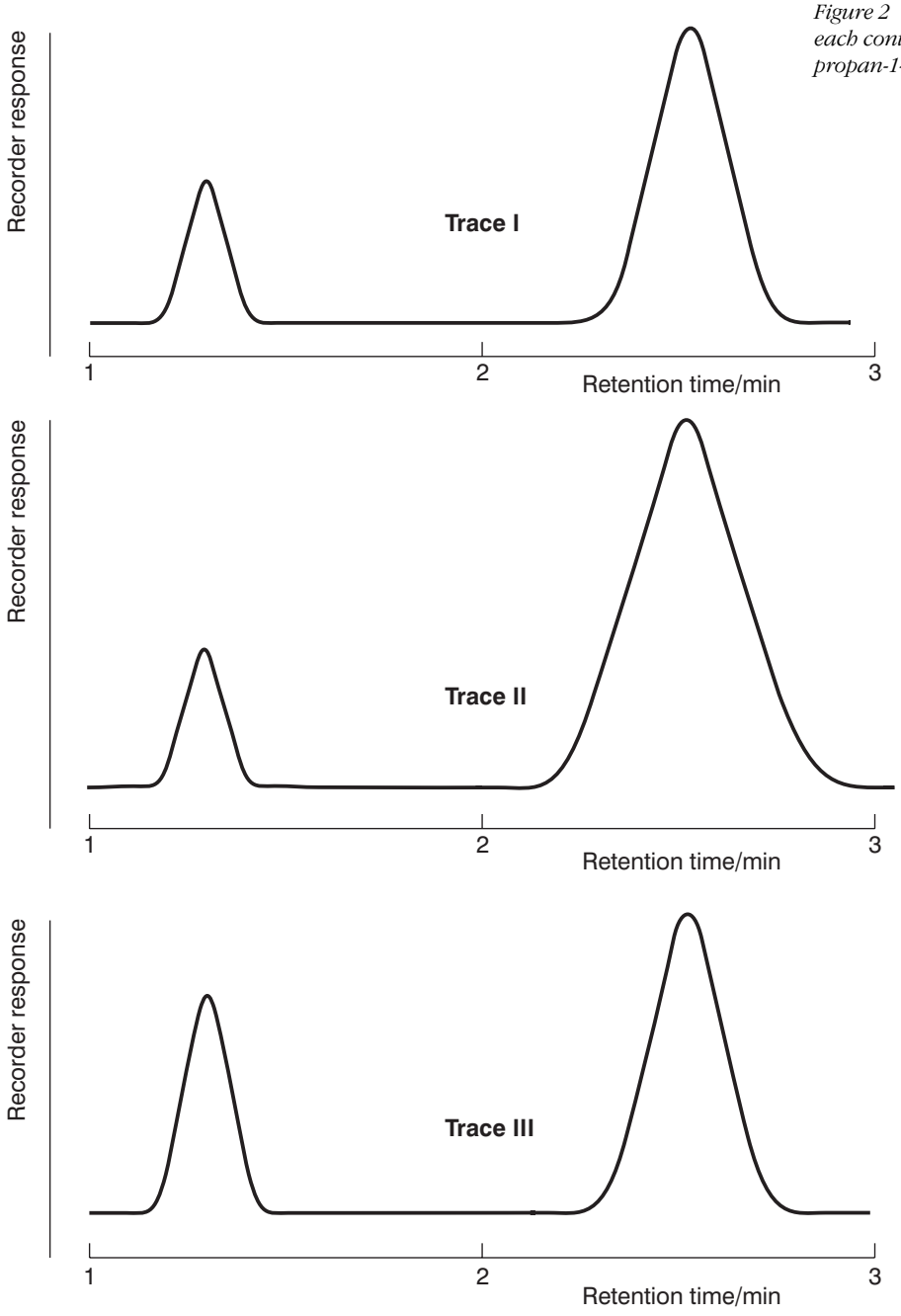


Figure 2 The g.l.c. traces of three blood samples each containing a standard amount of propan-1-ol

c Calculate the ratio of peak areas (ethanol peak : propan-1-ol peak) in trace I.

d Calculate the peak area ratios in traces II and III. Hence calculate BAC values for the other two blood samples. Was either over the limit?

e Suggest a reason why propan-1-ol is chosen for the standard rather than any of the other alcohols represented in Figure 1.

MD3.1

Making a toolkit of organic reactions

This activity will help you to revise and use some of the organic reactions you have met in the course.

What you do

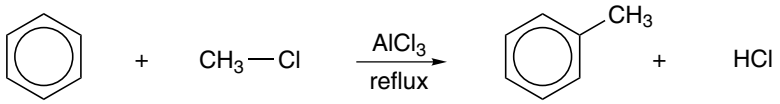
The idea is to organise some of the reactions you have met in the course, together with a few new ones, into a 'toolkit' of reactions which you can use to design organic syntheses.

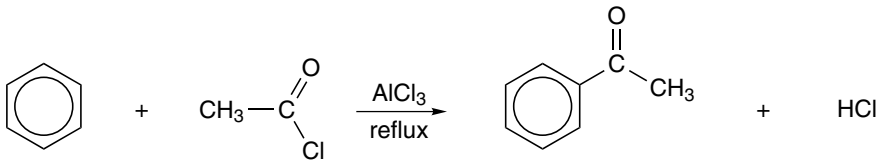
1. First make sure that you are familiar with the main reactions of the functional groups that you have met throughout the course. These are summarised in **Chemical Ideas 14.2.**
2. Read the **Reference section** below about useful synthetic reactions. This gives you some hints about making new C–C bonds as well as some extra reactions which are often useful in synthesis. *You are not expected to remember these extra reactions, but you should be able to use them correctly if you are given them.*
3. Then use the new reactions in the reference section, together with the more familiar ones you have met in earlier units, to complete the two flow sheets, **Chart A** and **Chart B**. These two flow sheets make up your 'toolkit'. To complete them, you should write the reaction conditions over each arrow and, where possible, the *reaction type* (substitution, oxidation, acylation, etc.) under the arrow.
4. Use the toolkit to answer the questions on page 315.

Reference section: Some useful synthetic reactions

When you design a synthesis, many of the reactions you will use will simply convert one functional group into another. But if you want to extend the carbon framework of the molecule and build up larger compounds, you need some way of making carbon–carbon bonds.

One way to do this is to use the Friedel-Crafts alkylation and acylation reactions:

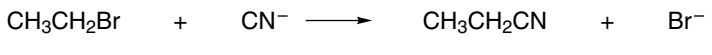




The C=O group can be modified further if necessary

These reactions are very useful because they provide a method of building side-chains onto a benzene ring.

A good way of *extending* a carbon chain is to use the reaction of cyanide ions, CN^-, with halogenoalkanes. The cyanide ion is a powerful nucleophile and will displace the halogen atom in much the same way as OH^-. For example:



propanenitrile

The reaction is carried out by refluxing the halogenoalkane with a solution of sodium cyanide in ethanol and water. The product is a *nitrile*.

Compare that reaction with this:

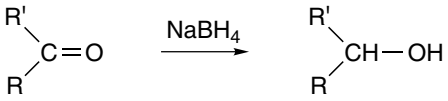
$$CH_3CH_2Br + OH^- \longrightarrow CH_3CH_2OH + Br^-$$

Nitriles themselves have few direct uses, but they are very important as synthetic intermediates. The important thing is that a new carbon–carbon bond has been made, and the nitrile group can then undergo further reactions. For example, when nitriles are hydrolysed with dilute acids, carboxylic acids are formed.

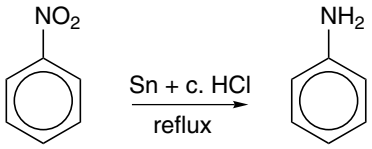
$$CH_3CH_2CN \xrightarrow[\text{reflux}]{H^+(aq)\ /\ H_2O} CH_3CH_2COOH$$

Sometimes it is necessary to reduce aldehydes and ketones back to alcohols. This does not take place readily and requires a powerful reducing agent. A complex metal hydride is used, called sodium tetrahydridoborate(III), $NaBH_4$:

$$RCHO \xrightarrow{NaBH_4} RCH_2OH$$



A different reducing agent, tin in the presence of concentrated hydrochloric acid, is used to convert nitro-groups into amino-groups:

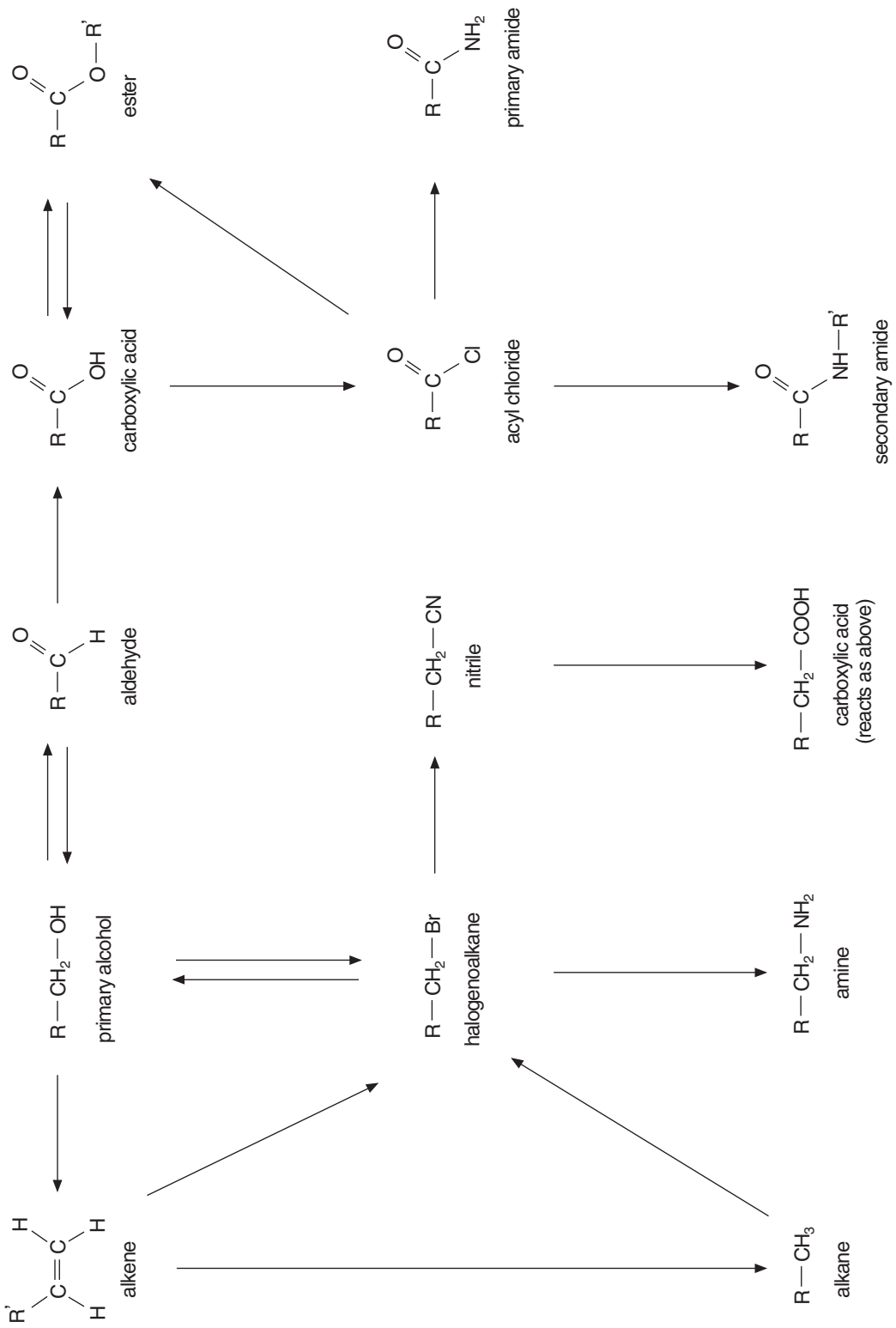


One final reaction. You will find that *acyl chlorides* are very useful synthetic intermediates. These can be made from carboxylic acids by refluxing with a reactive liquid called sulphur dichloride oxide (SCl_2O). The reaction mixture must be completely dry.

$$CH_3COOH + SCl_2O \longrightarrow CH_3COCl + SO_2 + HCl$$

Note You should be familiar with Friedel-Crafts alkylation and acylation reactions (see **Chemical Ideas 12.4** and **14.2**) and the reduction of aldehydes and ketones (see **Chemical Ideas 13.7** and **14.2**). You are not expected to remember the rest of the reactions in this reference section, but you should be able to use them correctly if you are given them.

The toolkit: Chart A



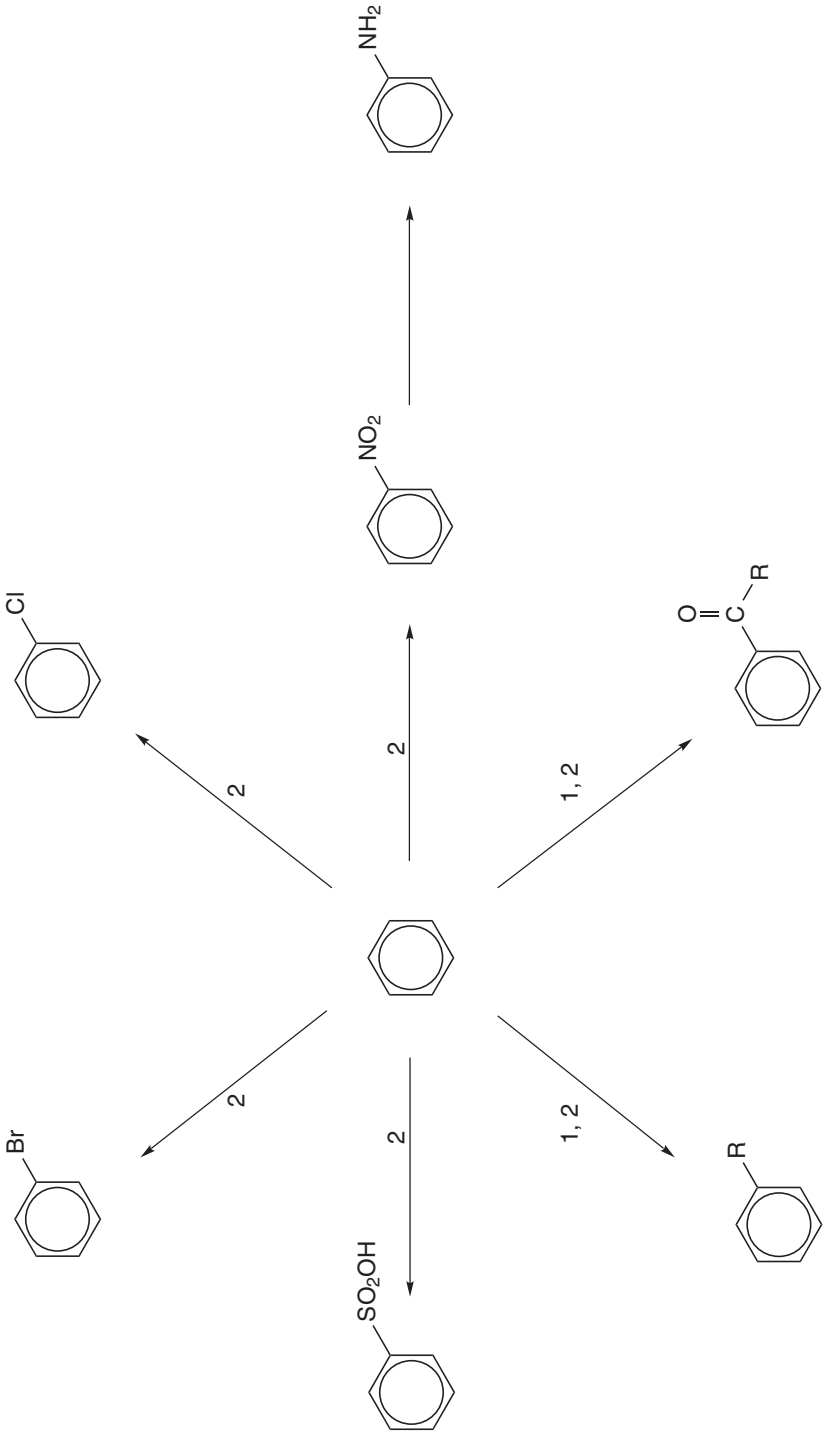
Notes

1 The formation of a nitrile from a halogenoalkane is a *carbon–carbon bond-forming reaction.*
The carboxylic acid formed from the nitrile has an extra carbon atom in the side-chain.
All other reactions are simple *functional group interconversion.*

2 The halogenoalkane shown will only be a minor product of the reaction from the alkene. The main product will be the isomer with the Br atom attached to the second carbon atom.

3 You may wish to add other reactions to this toolkit, for example, the formation of a secondary alcohol from an alkene, RCH = CHR', and a ketone from a secondary alcohol.

The toolkit: Chart B



Notes

1 The Friedel-Crafts reactions are *carbon–carbon bond-forming reactions.*

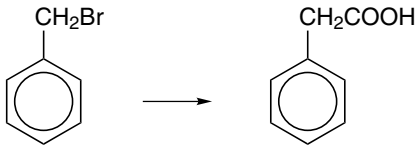
2 All the substitution reactions of arenes are *electrophilic.*

QUESTIONS

a Use the toolkit to design some simple two-step syntheses. In each case, write out the synthesis in the form of a flowchart and write the reagents and conditions on the arrows.

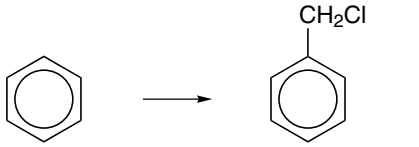
i $CH_3CH_2CH_2OH \longrightarrow CH_3CHBrCH_3$

ii



iii $CH_3CH_2COOH \longrightarrow CH_3CH_2CONH_2$

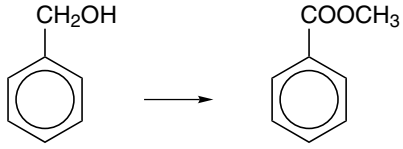
iv



v $CH_3CH_2OH \longrightarrow CH_3CH_2NH_2$

b Now, see whether you can work out routes for the following conversions. You should be able to carry out each conversion in no more than three steps. You have a supply of methanol in addition to the starting material, but no other organic compounds.

i

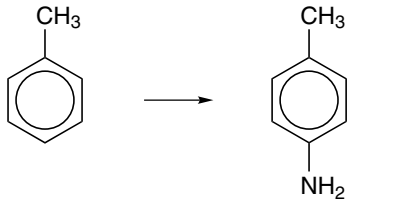


ii $CH_3CH{=}CHCH_3 \longrightarrow CH_3{-}\underset{\displaystyle COOH}{\underset{|}{CH}}{-}CH_2CH_3$

iii $CH_3CH_2CH_2Br \longrightarrow CH_3CH_2CH_2COOCH_3$

iv $CH_3CH_2OH \longrightarrow HOCH_2CH_2OH$

v



c Starting from ethene, work out a synthetic route for the preparation of the amide $CH_3CH_2CONHCH_2CH_3$ (six steps). You may not use any other organic compound.

MD3.2

Classifying reactions

This activity is based on the toolkits produced from Activity MD3.1 and will enable you to familiarise yourself with them.

What you do

Complete the table below by listing, for each type of reaction, one or more homologous series that undergo this reaction. Draw the functional group and give a balanced equation for an example of the reaction.

Type of reaction		Name of homologous series	Functional group	Example of reaction
Hydrolysis	**i** **ii** **iii**	Ester		$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$
Esterification	**i**			
Elimination	**i**			
Acylation	**i** **ii** **iii** **iv**			
Addition electrophilic nucleophilic	 **i** **ii**			
Substitution radical electrophilic nucleophilic	 **i** **ii** **iii**			
Oxidation	**i** **ii**			
Reduction	**i** **ii**			

QUESTIONS

a Name each of the homologous series in your table that can act as an acid.

b Name a homologous series that can act as a base.

c What types of organic compound have hydrogen bonding as the main intermolecular force?

d Give two different reducing agents used in organic reactions and give examples of these reactions.

e Both sodium cyanide and hydrogen cyanide are extremely toxic. Why are they still used in organic synthesis?

MD3.3

Using the toolkit to synthesise medicines

In this activity you will use your knowledge of organic reactions to devise ways of synthesising some complex organic molecules.

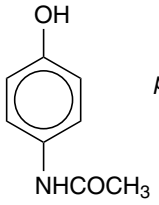
You will also see how spectroscopy can be used to monitor the chemical reactions under investigation.

What you do

In Parts 1 and 2, you will use the toolkit of organic reactions from **Activity MD3.1** to help you suggest synthetic routes for the preparation of two medicines, paracetamol and ibuprofen. In Part 3, you will use spectra to identify some of the organic molecules used in the synthesis of ibuprofen, and in Part 4, you will study the structure of some sex hormones.

Part 1: Making paracetamol from phenol

Paracetamol is widely used as a painkiller and to reduce fever. It is more expensive than salicylates like aspirin, but it is thought to have fewer side-effects in normal use. (Overdosing with paracetamol, however, can lead to irreversible liver damage.) You may remember looking at the n.m.r. spectrum of paracetamol in **Activity EP2.3**.



paracetamol

1 Use your toolkit to plan a synthesis of paracetamol from phenol. You should be able to do this in three steps. Write out your proposed scheme in the form of a flowchart. Write the reagents and conditions for each step above the arrows.

2 Indicate any stages where a reaction produces more than one isomer, such that the required product would have to be separated.

QUESTIONS

a Write out the *full* structural formula of the target molecule.

b For each step in your synthesis, choose a word from the list below to describe the *type of reaction* occurring:

substitution	oxidation	esterification
elimination	reduction	hydrolysis
addition	ethanoylation	polymerisation

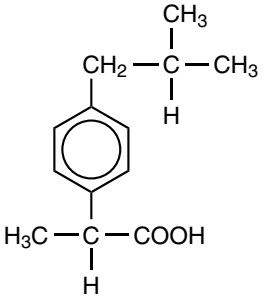
c Paracetamol is a white crystalline solid which melts at 169 °C. It is fairly soluble in hot water but insoluble in cold water. Explain how you could purify your product.

d Describe one way in which you could test whether your sample was pure paracetamol.

Part 2: Making ibuprofen from benzene

Over one million people in the UK are afflicted with rheumatoid arthritis, a disease in which their joints become painfully inflamed.

An early successful anti-inflammatory agent was a derivative of phenylpropanoic acid, called *ibuprofen*, which was introduced by Boots (now Knoll Pharmaceuticals) in the 1970s. It has also proved to be a safe and effective analgesic. Since 1983 it has been available from pharmacists as a non-prescription drug, sold under several tradenames. Its systematic name is 2-(4-(2-methylpropyl)phenyl) propanoic acid.



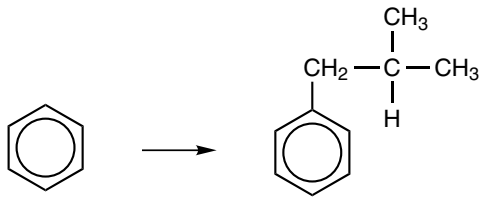
ibuprofen

3 Use your toolkit to devise a synthesis of the target molecule, ibuprofen, from benzene. You can use other simple organic molecules in your synthesis. It is quite complex (six steps) and, if you get stuck, you may find it helps to work through the following stages.

Help – if you need it

Start by comparing the structures of benzene and ibuprofen. Two **carbon–carbon bond-forming reactions** will be necessary to attach the two side-chains to the benzene ring. A Friedel-Crafts alkylation will enable the hydrocarbon side-chain to be attached directly, and if this is followed by Friedel-Crafts acylation at the 4-position in the benzene ring, the second side-chain can be added. This side-chain contains a reactive group which can be converted into the target molecule by a series of **functional group interconversions**.

Step 1: Attaching the alkyl side-chain

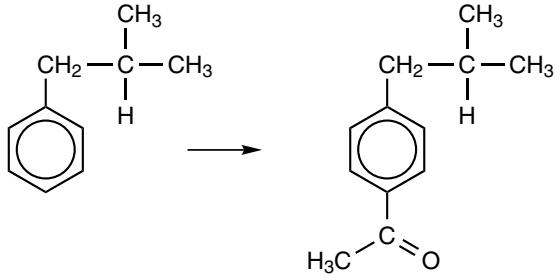


e Give the structure and name of the halogenoalkane needed for this Friedel-Crafts alkylation reaction.

f Classify this reaction by stating the type of reagent involved and the type of reaction.

g What catalyst is needed and how does it help the reaction?

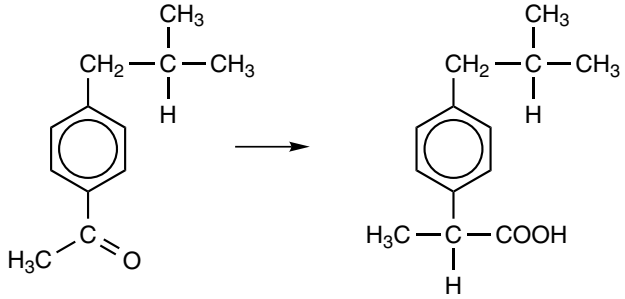
Step 2: Attaching an acyl side-chain



h What is the name and structure of the acyl chloride needed for this Friedel-Crafts acylation?

i What catalyst should be used?

Steps 3–6: Converting the acyl side-chain into a phenylpropanoic acid



j What *carbon–carbon bond-forming* reaction could be used to introduce a new functional group which could easily be changed to a carboxylic acid group?

k What key intermediate must be prepared from the ketone before this reaction can take place?

l What functional group must first be obtained from the ketone before the key intermediate can be prepared?

m Now write a total synthesis of the target molecule, giving the reaction conditions necessary for each step above the arrow linking the intermediates. Where possible, classify the reactions according to reagent and reaction type beneath the arrow.

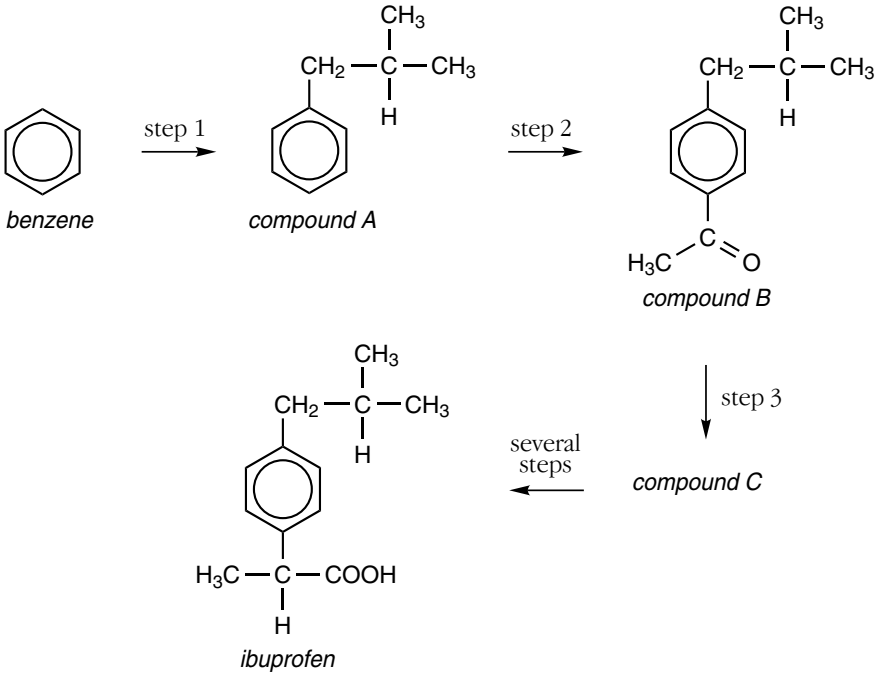
n The synthesis of a new medicine must be accompanied by the correct stereochemistry. This may be crucial to the medicine's action in the body. Place an asterisk (*) against any chiral carbon atom present in the target molecule.

Part 3: Analysing spectra

In this part of the activity you will analyse the infrared, nuclear magnetic resonance and mass spectra of some organic molecules used in the synthesis of the medicine ibuprofen.

You will need to refer to the charts of characteristic i.r. absorption frequencies and proton n.m.r. chemical shifts in the **Data Sheets**.

As you have seen in Part 2 of this activity, a possible synthesis of ibuprofen could involve the following route.



The i.r., n.m.r. and mass spectra of compounds A, B, C and ibuprofen are given in Figures 1, 2, 3 and 4, respectively. You will need to refer to these to answer the questions below.

QUESTIONS

o For compound A:

- **i** Why are there several peaks at around 3000 cm^{-1} in Figure 1(a)?
- **ii** Identify the hydrogen atoms responsible for each of the signals in Figure 1(b).
- **iii** Identify the ions responsible for the peaks at mass 134 and 91 in Figure 1(c). Why has the peak at mass 135 an abundance of about 10% of the peak at mass 134?

p Identify and explain the main changes that have occurred to the i.r., n.m.r. and mass spectra during step 2 of the synthesis, i.e. the conversion of compound A, in Figures 1(a), 1(b) and 1(c), to compound B, in Figures 2(a), 2(b) and 2(c).

q **i** By comparing the spectra for compound C, in Figures 3(a), 3(b) and 3(c), with those of compound B, deduce the structure of compound C.

ii What type of reaction is involved in step 3, the conversion of B to C?

r The spectra for ibuprofen, in Figures 4(a), 4(b) and 4(c), are quite complex. Identify, with reasons, as many of the main features of these spectra as possible.

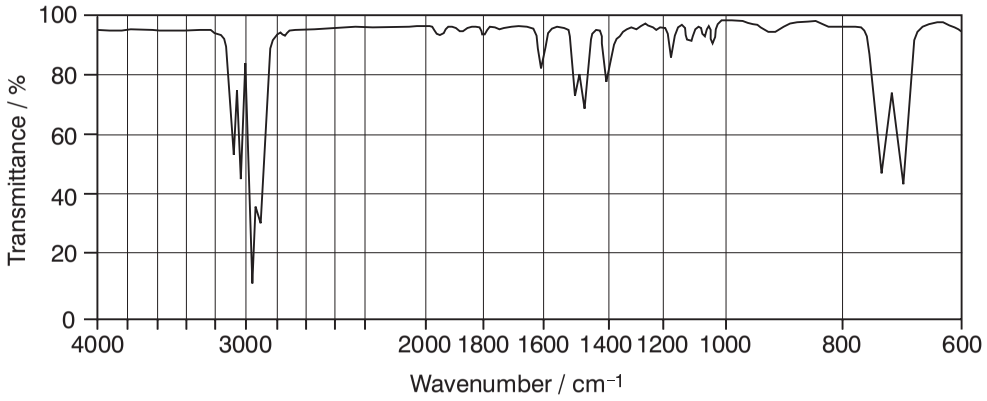


Figure 1(a) The i.r. spectrum of A (in the gas phase)

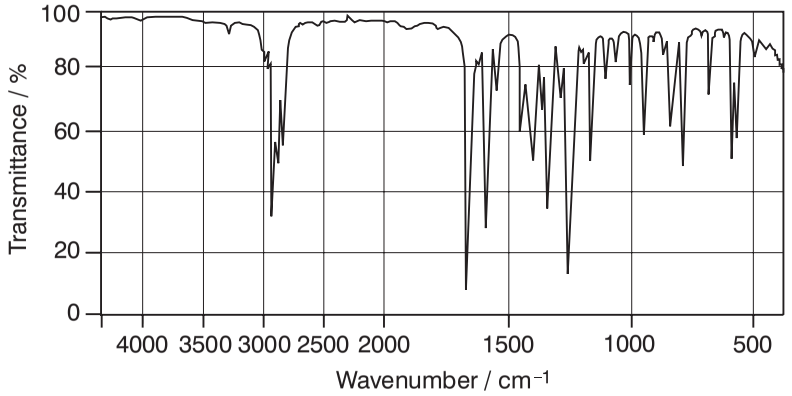


Figure 2(a) The i.r. spectrum of B (in solution)

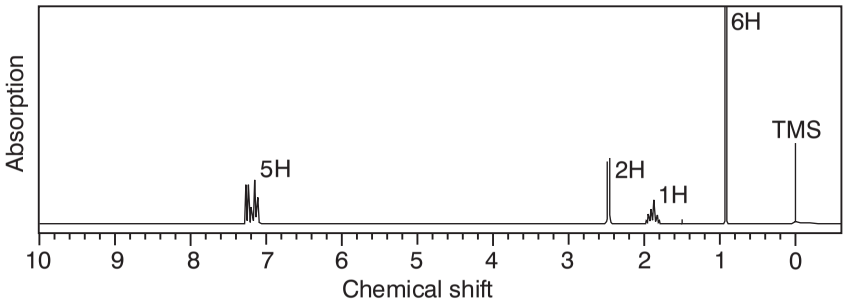


Figure 1(b) The n.m.r. spectrum of A

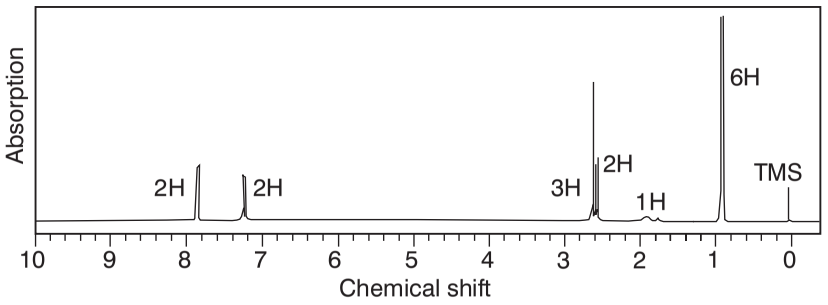


Figure 2(b) The n.m.r. spectrum of B

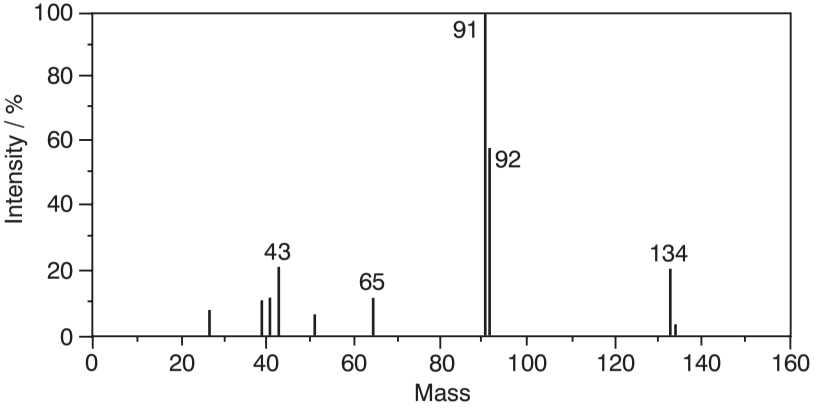


Figure 1(c) The mass spectrum of A

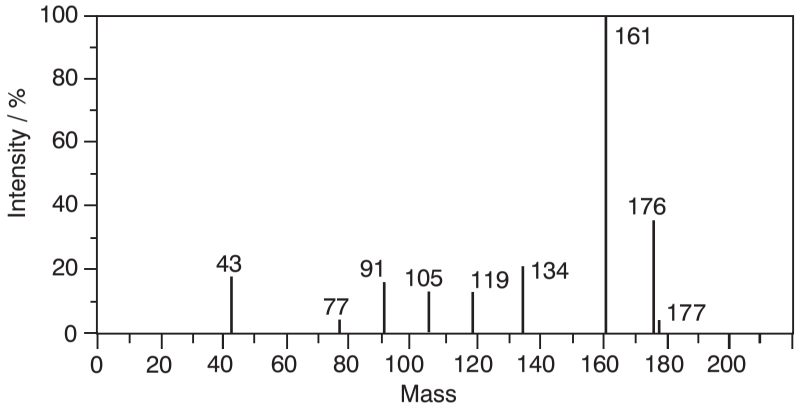


Figure 2(c) The mass spectrum of B

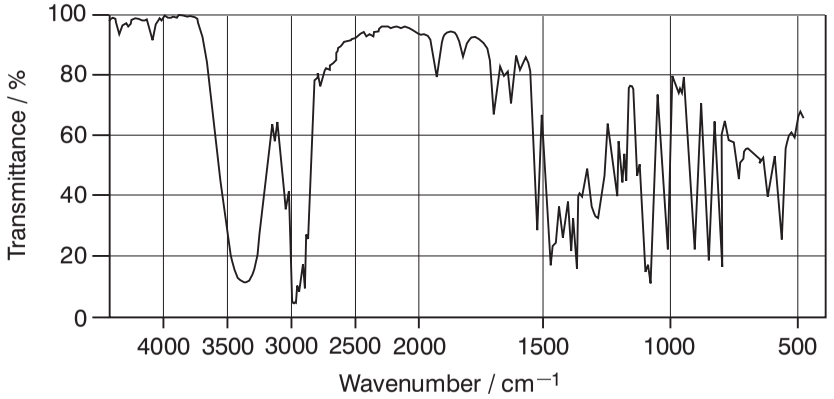


Figure 3(a) The i.r. spectrum of C (in solution)

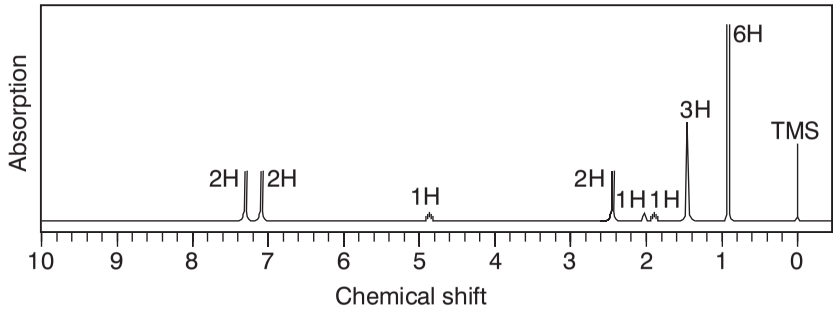


Figure 3(b) The n.m.r. spectrum of C

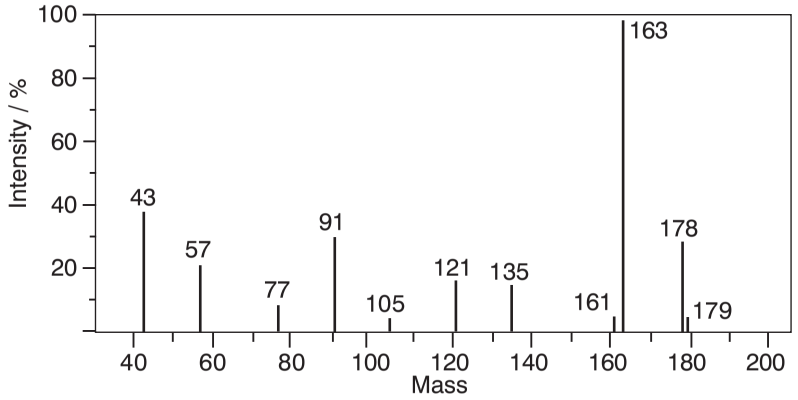


Figure 3(c) The mass spectrum of C

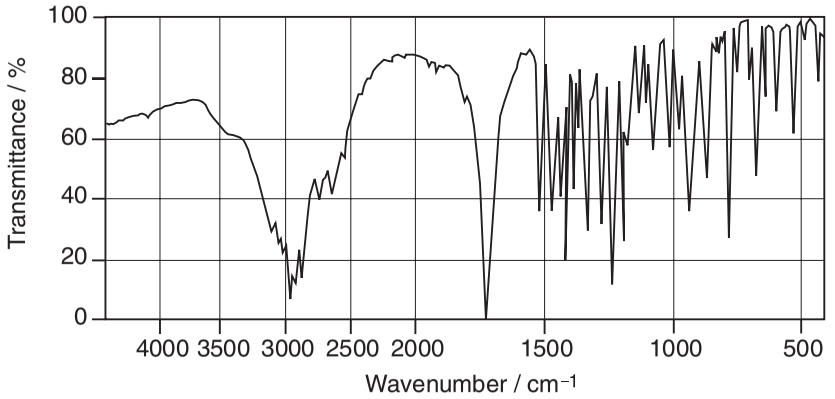


Figure 4(a) The i.r. spectrum of ibuprofen (in solution)

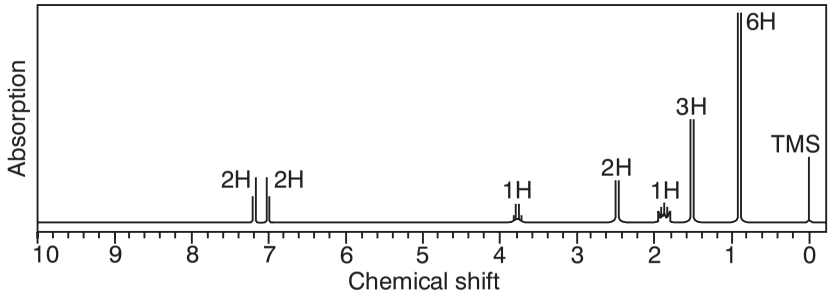


Figure 4(b) The n.m.r. spectrum of ibuprofen

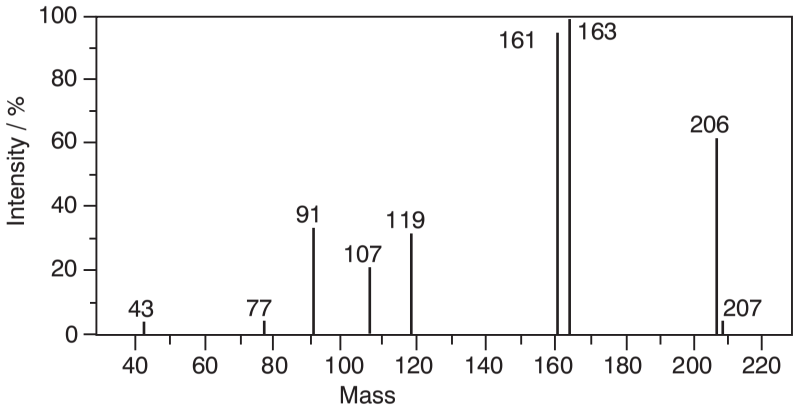
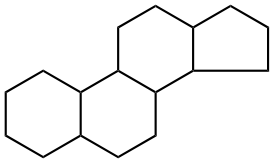


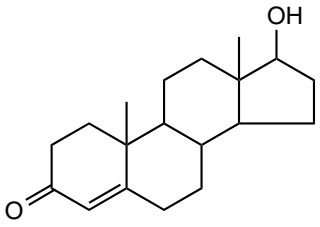
Figure 4(c) The mass spectrum of ibuprofen

Part 4: Investigating sex hormones

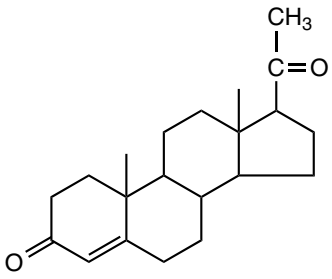
The *sex hormones* are steroids. They each contain the same carbon framework of four fused rings.



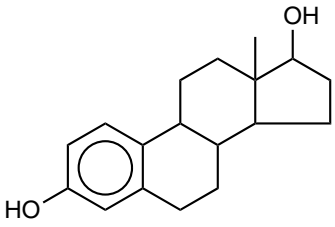
the steroid ring system



testosterone



progesterone



oestradiol

The male sex hormone, *testosterone*, is secreted in the testes and controls the development of secondary sexual characteristics at puberty and sexual activity in the adult.

Oestradiol is one of the principal female sex hormones controlling secondary sexual characteristics. It belongs to a group of female sex hormones called *oestrogens*. *Progesterone* is a second type of female steroid hormone. Its main function is to prepare the wall of the uterus for implantation of a fertilised ovum.

Contraceptive pills usually contain a combination of an oestrogen and progesterone. High levels of these two hormones suppress normal monthly ovulation; this is the natural mechanism used by the body to suppress ovulation during pregnancy.

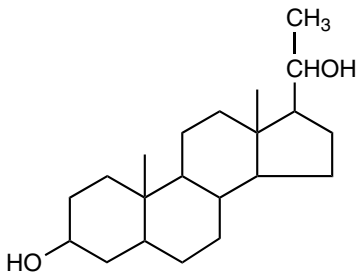
QUESTIONS

s Is the alcohol functional group in oestradiol primary, secondary or tertiary?

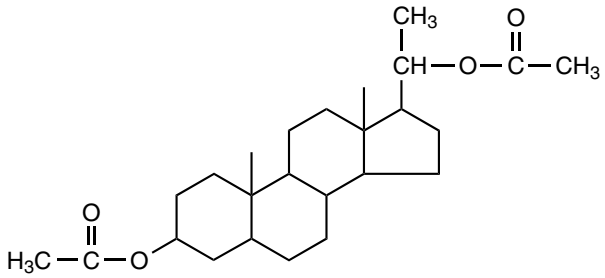
t Explain how a simple test-tube reaction using $FeCl_3$ solution could be used to distinguish between testosterone and oestradiol.

u As a synthetic chemist you wish to modify the progesterone structure in the hope of finding safer, more effective birth-control pills. Use your toolkit to show how you could make the following compounds from progesterone.

i

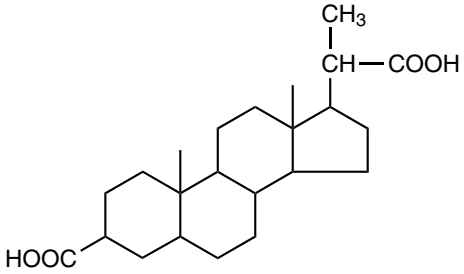


ii



Synthesise the molecule above from your product in **u i** in one step.

iii



Synthesise the molecule above from your product in **u i** in three steps.

v A steroid compound was known to be a female sex hormone. It was thought to be either progesterone or oestradiol.

The infrared spectrum of the steroid is shown in Figure 5. Use the chart of i.r. absorption frequencies in the **Data Sheets** to help you decide on the possible identity of the hormone. Give reasons for your decision.

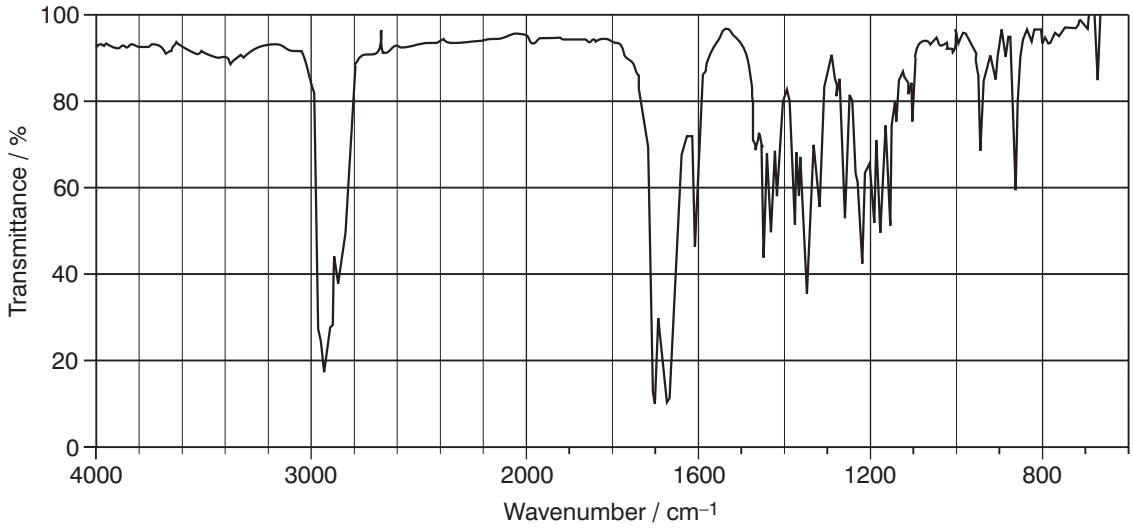


Figure 5 The i.r. absorption spectrum of the unknown steroid (in CCl_4 solution)

MD3.4

Manufacturing salbutamol (Optional extension)

***This activity looks in more detail at the reaction sequence which is used to make salbutamol, and at how much the chemicals used in its synthesis contribute to its cost. The infrared, nuclear magnetic resonance and mass spectra of these compounds are also analysed. There is more about salbutamol in* Chemical Storylines MD3.**

Part 1: Costing salbutamol

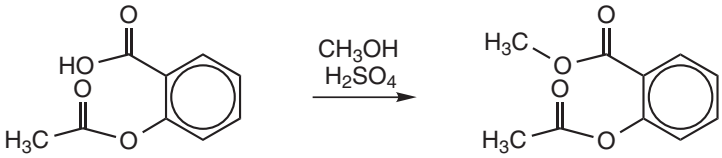
When designing a synthetic route for a new medicine, chemists in the pharmaceutical industry need to bear in mind the following points:

- The starting material should be cheap and readily available.
- The route should involve as few steps as possible, for speed and because every step involves some loss of material.
- Yields should be high for each step.
- Inexpensive and safe reagents and solvents should be used.
- Purification should be easy – medicines must not contain contaminants.

A possible synthesis of *salbutamol* begins with aspirin and involves five steps. The yields for these steps are high compared with many reactions in organic chemistry. Although the final step has a yield of 30% it should be remembered that 30% of the inactive isomer is also formed. The reaction sequence contains no unusual materials.

Reaction sequence

Step 1

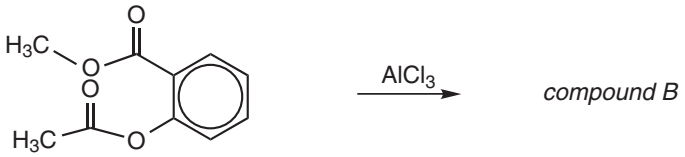


aspirin *compound A*

Solvent	Other reagent
methanol 10% w/v solution	sulphuric acid 10 g per kg aspirin

(w/v means weight (mass) of solute : volume of solvent. A solution containing 100 g of solute in 1 dm^3 of solvent would be a 10% w/v solution. In this case, the solute is aspirin and the solvent is methanol.)

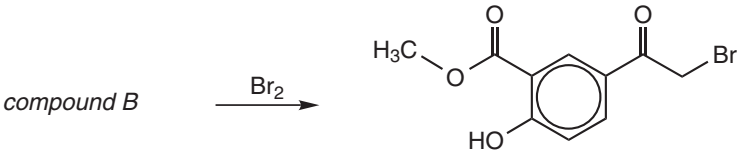
Step 2



compound A *compound B*

Solvent	Other reagent
nitrobenzene 10% w/v solution	aluminium chloride 1 mole per mole of A

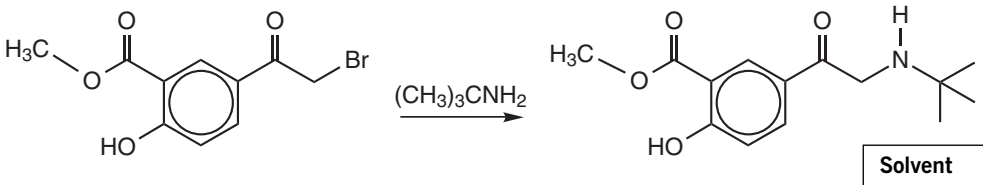
Step 3



compound C

Solvent	Other reagent
trichloromethane 10% w/v solution	bromine 1 mole Br_2 per mole of B

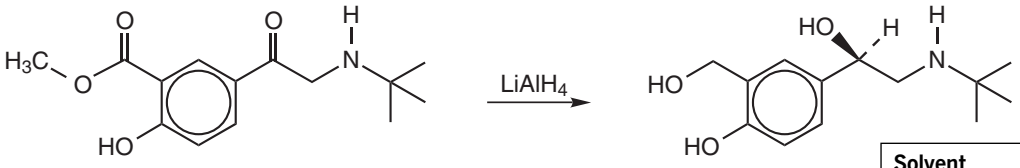
Step 4



compound C *compound D*

Solvent	Other reagent
trichloromethane 10% w/v solution	2-amino-2-methylpropane 2 moles per mole of C

Step 5



compound D

salbutamol (plus an equal amount of its optical isomer)

Solvent	Other reagent
ethoxyethane 2.5% w/v solution	lithium tetrahydridoaluminate 3 moles per mole of D

Costs

Solvents	Cost/£ dm^{-3}	Reagents	Cost/£ kg^{-1}
methanol	4.20	aspirin	12.80
nitrobenzene	9.30	sulphuric acid	2.17
trichloromethane	10.70	aluminium chloride	11.20
		bromine	13.20
ethoxyethane	6.00	2-amino-2-methylpropane	9.60
		lithium tetrahydridoaluminate	450.00

Economics of process

Table 1 gives the yields and relative molecular masses of the organic compounds in the reaction sequence.

1 Copy out Table 1 and complete the other entries to show the masses and amounts of these compounds which could be made *starting with 1 kg of aspirin*.

Compound	M_r	Yield/%	Mass produced/g	Amount produced/mol
aspirin	180	–	1000	5.56
A	194	85		
B	194	60		
C	273	75		
D	265	55		
salbutamol	239	30		

Table 1 Yields and quantities for salbutamol synthesis

2 Use information contained in the reaction sequence and in Table 1 to complete a copy of Table 2 to show the costs of the reagents and solvents used *to convert 1 kg of aspirin into salbutamol*.

Reagent/solvent	Quantity required	Cost/£
aspirin	1 kg	
methanol		
sulphuric acid		
nitrobenzene		
aluminium chloride		
trichloromethane		
bromine		
2-amino-2-methylpropane		
ethoxyethane		
lithium tetrahydridoaluminate		
	Total cost	

Table 2

3 You now know the cost of converting 1 kg of aspirin into salbutamol. What is the cost of synthesising 1 kg of salbutamol?

QUESTIONS

a What other costs will be involved in the production of salbutamol?

b What percentage of the cost of making salbutamol is from the use of solvents? Suggest how this cost may be reduced.

Part 2: Spectra of compounds involved in the synthesis of salbutamol

The product from each stage of the synthesis of salbutamol can be characterised by the use of infrared (i.r.) and nuclear magnetic resonance (n.m.r.) spectroscopy and mass spectrometry.

The i.r., n.m.r. and mass spectra of aspirin, compounds A, B and C (from the reaction sequence on pages 324–5), and salbutamol are given in Figures 1–5.

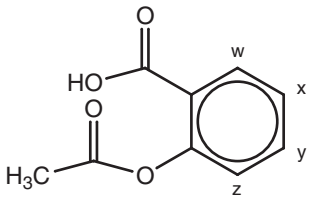
QUESTIONS

For some of the following questions, you will need to refer to the tables of characteristic i.r. absorption frequences and proton n.m.r. chemical shifts in the **Data Sheets**.

c For the starting material in this synthesis, aspirin (2-ethanoylhydroxybenzoic acid):

i identify the bonds responsible for the broad peak around 3000 cm^{-1}, and the sharp peaks at 1750 cm^{-1} and 1690 cm^{-1} in Figure 1(a).

ii identify the hydrogen atoms responsible for the signals at chemical shifts 2.2. and 13.1 in Figure 1(b). The hydrogen atoms responsible for the cluster of signals in the chemical shift range 7.5 ± 0.5 are indicated as w, x, y and z on the following structure of aspirin.



iii identify the ions responsible for the peaks at mass 180, 163, 120 and 43 in Figure 1(c).

d Compare Figures 1(a)–1(c) and Figures 2(a)–2(c). Identify and explain the main changes that have occurred to the i.r., n.m.r. and mass spectra during the conversion of aspirin into compound A in step 1.

e **i** Compound B and compound A both have molecular ion peaks of mass 194. How are compounds B and A related?

ii With the help of the relevant spectra, Figures 3(a)–3(c), deduce the structure of compound B.

f **i** Compare Figure 3(b) and Figure 4(b). Identify and explain the main change that has occurred to the n.m.r. spectrum in the conversion of compound B into compound C in step 3.

ii In the mass spectrum of compound C, Figure 4(c), there are *two* molecular ion peaks of equal intensity, at mass 272 and 274 respectively. Explain this observation.

g The n.m.r. spectrum of salbutamol is given in Figure 5. This also shows the integrated trace, which goes upward in steps. The height of each step in the trace is proportional to the number of hydrogen atoms absorbing at the chemical shift. Suggest which signals correspond to which hydrogen atoms in the salbutamol molecule and give reasons for your choice.

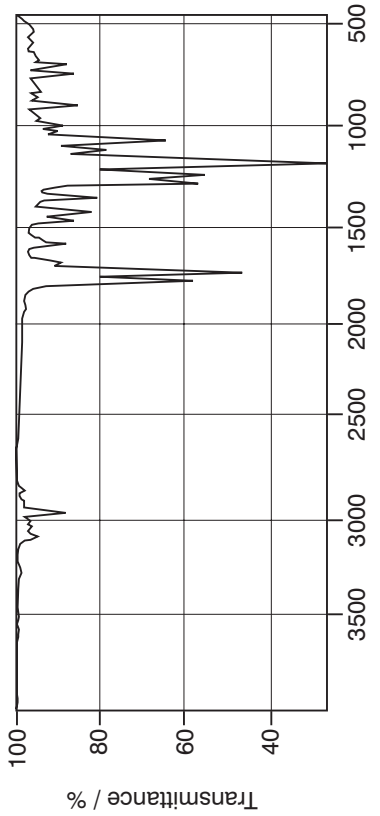


Figure 2(a) The i.r. spectrum of compound A (in the gas phase)

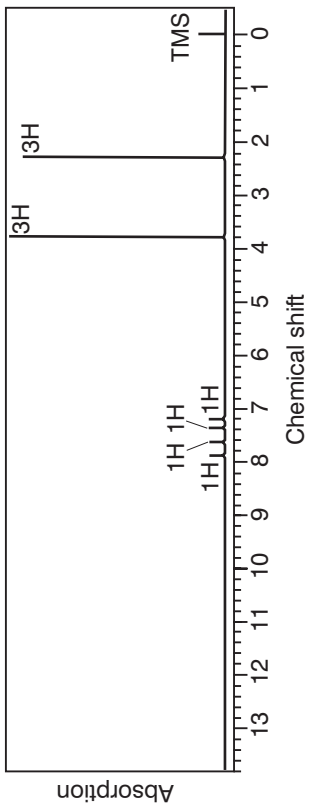


Figure 2(b) The n.m.r. spectrum of compound A

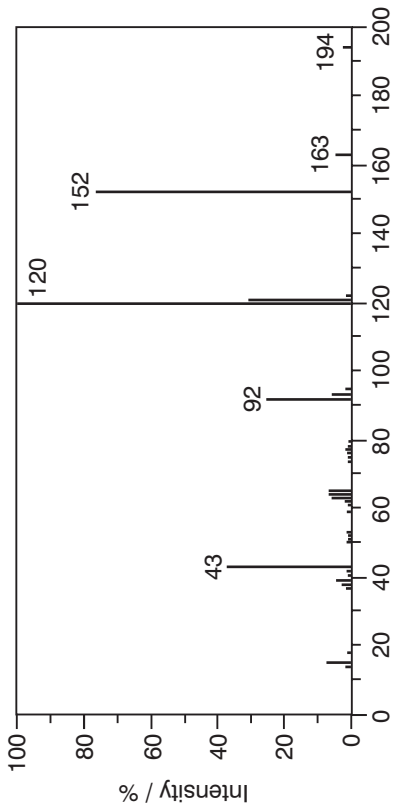


Figure 2(c) The mass spectrum of compound A

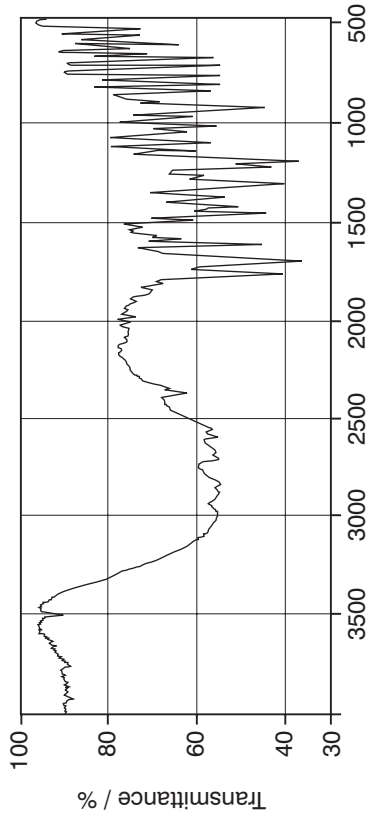


Figure 1(a) The i.r. spectrum of aspirin (in solution)

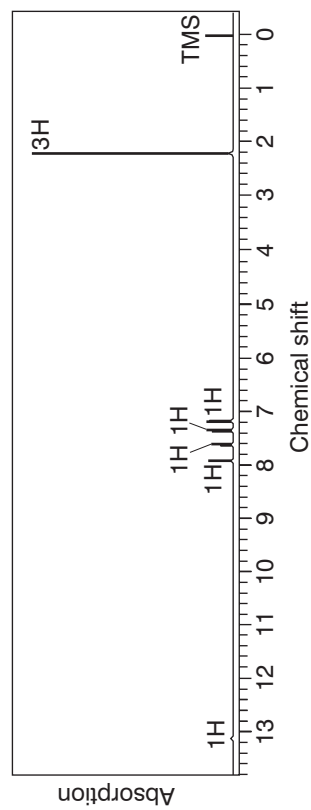


Figure 1(b) The n.m.r. spectrum of aspirin

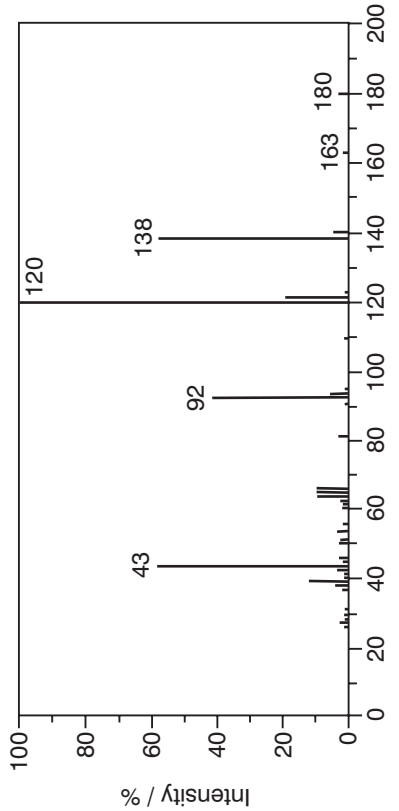


Figure 1(c) The mass spectrum of aspirin

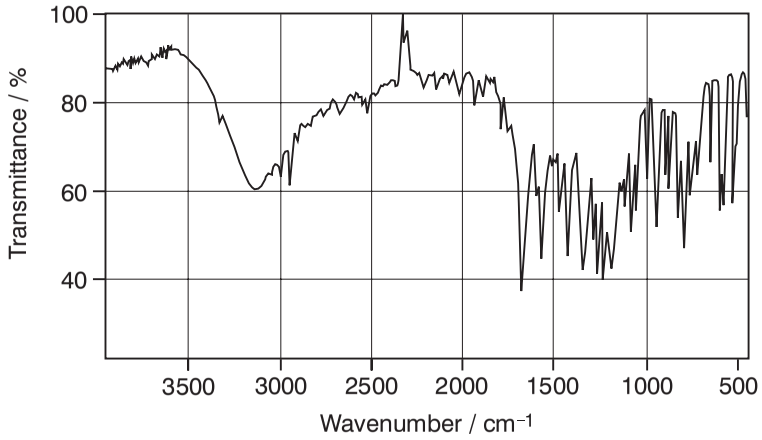


Figure 3(a) The i.r. spectrum of compound B (in solution)

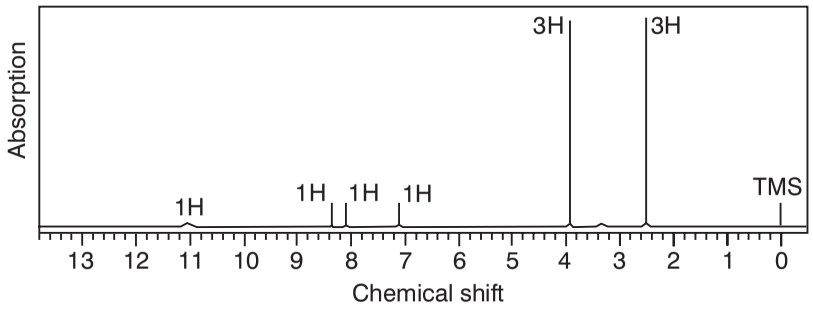


Figure 3(b) The n.m.r. spectrum of compound B (in solution)

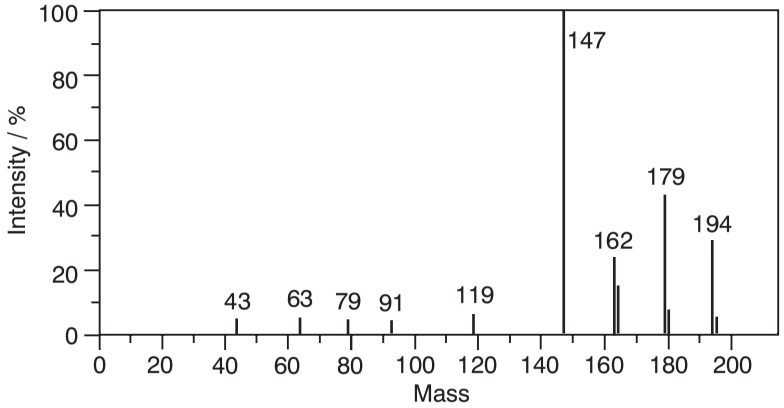


Figure 3(c) The mass spectrum of compound B (in solution)

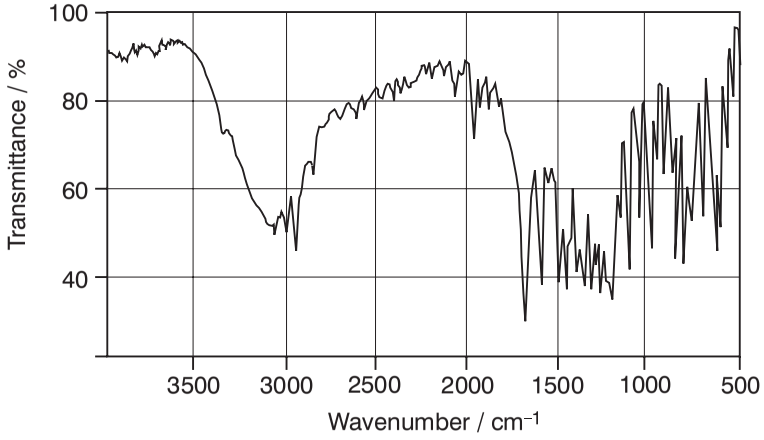


Figure 4(a) The i.r. spectrum of compound C (in solution)

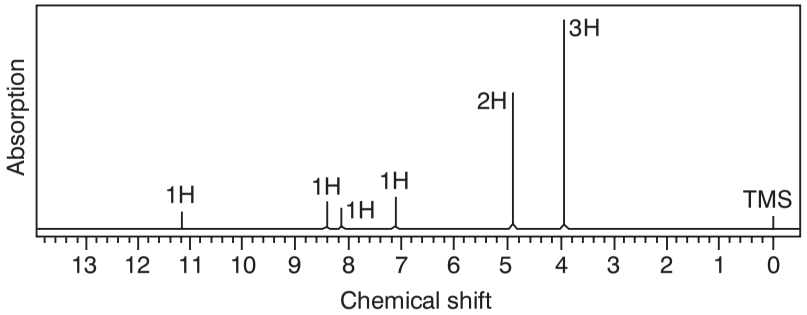


Figure 4(b) The n.m.r. spectrum of compound C

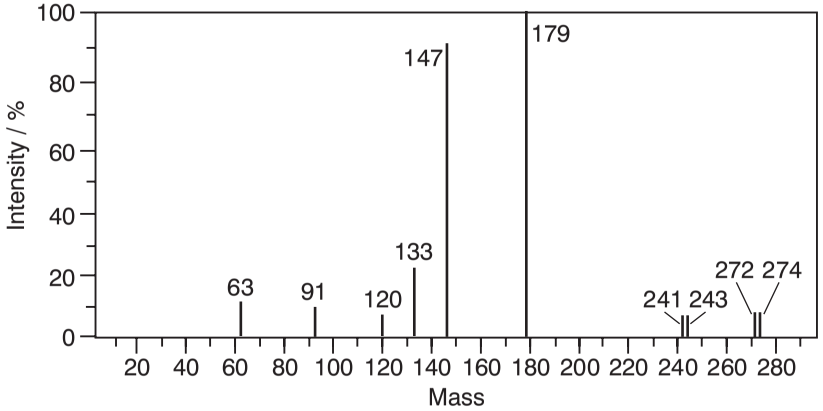


Figure 4(c) The mass spectrum of compound C

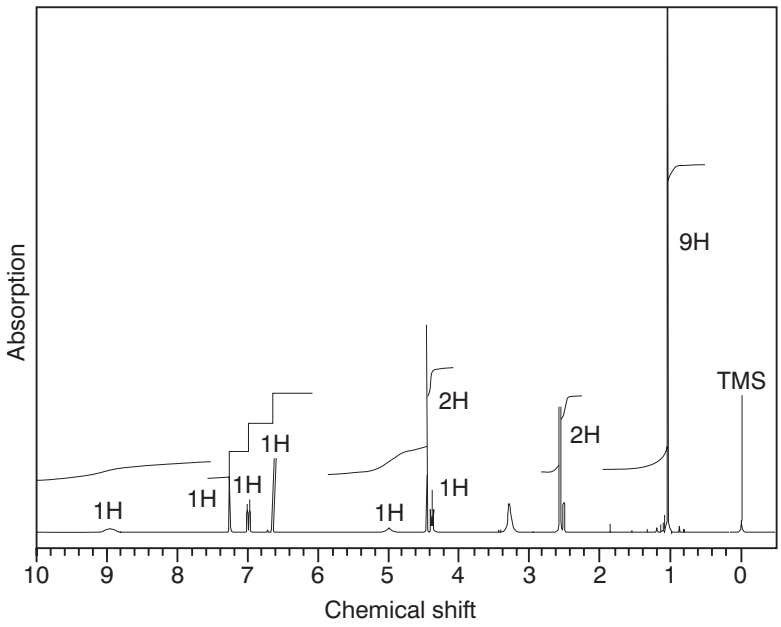


Figure 5 The n.m.r. spectrum of salbutamol

MD5.1

Making and testing a penicillin

In this activity you can use your skills in handling organic chemicals to prepare a semi-synthetic penicillin. You can then test your product for bacterial activity.

Requirements

- 100 cm^3 well-stoppered bottle (or conical flask)
- 6-aminopenicillanic acid (6-APA) (1.0 g)
- 25 cm^3 measuring cylinders (2)
- 10 cm^3 measuring cylinder
- sodium hydroxide solution, 1 mol dm^3 (5 cm^3)
- teat pipettes
- benzoyl chloride (0.5 cm^3)
- propanone (5 cm^3)
- test-tubes
- 100 cm^3 beakers (2)
- ethyl ethanoate (15 cm^3)
- glass rod (or magnetic stirrer)
- pH meter (or Universal Indicator paper)
- dilute hydrochloric acid, 1 mol dm^{-3} (10 cm^3)
- 50 cm^3 separating funnel
- saturated sodium hydrogencarbonate solution (25 cm^3)
- 4 agar plates impregnated with *Bacillus subtilis**
- cork borer (5–7 mm)
- ethanol (for sterilisation)
- beaker of disinfectant
- protective gloves
- adhesive tape
- small amounts of control solution for testing bacterial activity:
  - 6-APA solution (made by dissolving 0.13 g 6-APA in a solution of 0.15 g sodium hydrogencarbonate in 250 cm^3 water; take 10 cm^3 of this solution and dilute to 100 cm^3)
  - sodium benzoate solution (made by dissolving 0.13 g sodium benzoate in 250 cm^3 water; take 10 cm^3 of this solution and dilute to 100 cm^3 with water)

CARE Benzoyl chloride is corrosive and lachrymatory (it is a severe eye irritant) and must be used in a fume cupboard. It gives off fumes of hydrogen chloride gas in moist air. Wear gloves when measuring out, and use a pre-marked teat pipette.

CARE Propanone, ethyl ethanoate and ethanol are highly flammable liquids. Keep bottles stoppered when not in use, and well away from naked flames.

CARE Consult your teacher before handling the bacterial culture and follow the safety instructions carefully. Wear a lab coat and gloves all the time. Cover any skin cuts with effective waterproof dressings and wash your hands thoroughly at the end of the session. Report any spillages immediately. Any material which has come into contact with the bacterial culture must be sterilised before disposal, or before returning to stock cupboards. The sealed plates must be sterilised in a pressure cooker or autoclave before disposal.

benzoyl chloride

ethanol

ethyl ethanoate

propanone

sodium hydroxide solution

CARE Eye protection must be worn.

CARE 6-APA can act as a sensitiser by inhalation or skin contact. Wear protective gloves and do not inhale the dust.

CARE If you are allergic to penicillins, you should not do this activity.

* See instructions for preparation in the Teacher's and Technician's Guide

The reaction scheme

You will be supplied with 6-aminopenicillanic acid (6-APA). This is obtained from penicillin G, which is made naturally. 6-APA can be reacted with different acyl chlorides to produce a variety of new penicillins with different properties and a wide range of antibacterial activity.

Your task is to convert 6-APA into phenylpenicillin. You will not be able to isolate your product in pure form, but you will be able to test its activity against bacteria.

The reaction scheme you will use is shown in Figure 1.

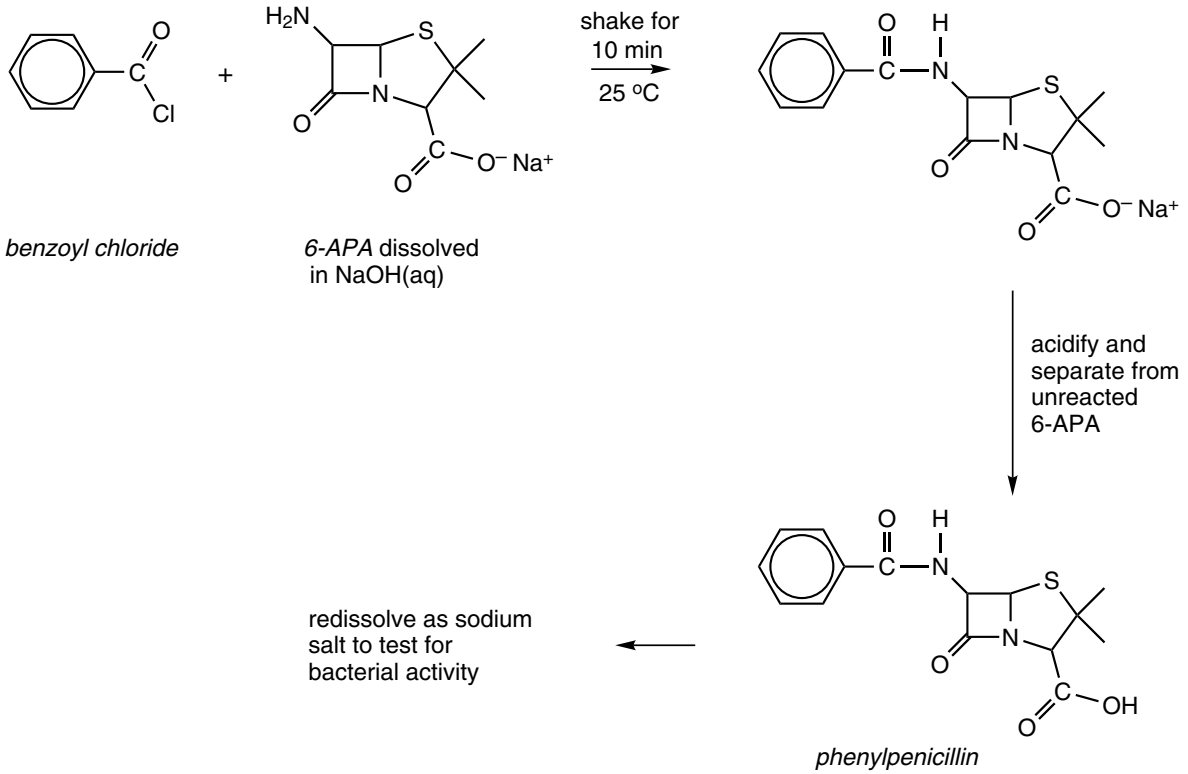


Figure 1 Reaction scheme for the synthesis of phenylpenicillin

Note that benzoyl chloride is a relatively unreactive acyl chloride and can be used in aqueous solution.

The 4-membered **lactam** ring is easily destroyed by strong acids and by alkalis. To reduce this hydrolysis reaction to a minimum, the pH of the solution is kept in the range pH 5–8 during the preparation. When you acidify the reaction mixture with hydrochloric acid during the purification procedure, the pH of the solution falls to pH 2, so you must work quickly at this stage.

As you go through the stages of the synthesis on page 332, use the column on the right-hand side to keep track of the changes taking place. Write the structure of the product where this has changed and a brief comment about what has happened at that stage. When you carry out the extraction with ethyl ethanoate to purify your product, make sure you know what is in each layer.

What you do

Part 1: Making and purifying the penicillin

Notes

1 Weigh out 1.0 g of 6-APA (**CARE** Wear protective gloves and do not inhale the dust) and mix it with 10 cm^3 of distilled water in a stoppered bottle (or conical flask).

2 Add 1 mol dm^{-3} of sodium hydroxide (**CARE** Irritant) drop by drop until a just-clear solution is obtained. This should take about 5 cm^3 of the sodium hydroxide solution.

3 In the fume cupboard, dissolve 0.5 cm^3 of the benzoyl chloride (**CARE** Corrosive and a severe eye irritant) in 5 cm^3 of propanone (**CARE** Highly flammable) in a clean, dry test-tube. Add this solution drop by drop, with swirling, to the dissolved 6-APA in the bottle. Stopper the bottle firmly and shake the mixture gently for about 10 minutes. (**CARE** You may need to release the pressure once or twice by easing off the stopper in a fume cupboard.)

4 Transfer the reaction mixture to a 100 cm^3 beaker and add 10 cm^3 of ethyl ethanoate (**CARE** Highly flammable). Using a pH meter (or pH paper) acidify the mixture with stirring, using 1 mol dm^{-3} hydrochloric acid. Add the acid until the pH of the solution falls to pH 2. (Any unreacted 6-APA forms a water-soluble hydrochloride. Phenylpenicillin is more soluble in organic solvents than water.)

5 Transfer both layers to a separating funnel and shake the mixture well. Separate into two 100 cm^3 beakers. Keep both layers. (The density of ethyl ethanoate is 0.90 g dm^{-3}. Make sure you know which layer is which.)

6 Return the aqueous layer to the funnel and add a further 5 cm^3 of ethyl ethanoate. Shake the mixture and separate it into the two beakers. You can now discard the aqueous layer down the fume-cupboard sink. (**CAUTION** Do not discard the wrong layer!)

7 Now add 10 cm^3 of water to the *organic* layer in the beaker. Adjust the pH to 6–7 by adding saturated sodium hydrogencarbonate solution. Transfer the mixture to the separating funnel and shake it well, taking care to release any build-up of pressure.

This time run the lower *aqueous* layer into a clean 25 cm^3 measuring cylinder. Add water to adjust the volume in the measuring cylinder to 25 cm^3 and stir well. This solution contains the phenylpenicillin you have made.

Part 2: Testing for antibacterial activity

Consult your teacher before handling the bacterial culture and **follow the safety instructions carefully**.

8 Take 1 cm^3 of your phenylpenicillin solution and dilute it to 10 cm^3 with distilled water. Stir well.

9 Dip the cork borer in ethanol in a beaker. **Hold the cork borer horizontally** so that flames do not pass up the centre and burn your hand. Pass the borer through a Bunsen flame to ignite the ethanol. Hold the borer to one side of the flame and allow the ethanol to burn off. This will heat the surface of the cork borer to about 60 °C so that it is sterilised. (**CARE** Make sure that the beaker containing the ethanol is not placed near the Bunsen flame. **Allow the cork borer to cool** before returning it to the ethanol beaker.)

10 Use the sterilised cork borer to make a well in the centre of an agar plate impregnated with *Bacillus subtilis,* by pressing the borer into the agar and then lifting out the cut plug of agar using a sterile spatula. (Flame the spatula in the same way as the cork borer.) Place the agar plug straight into a beaker of disinfectant. Re-flame the cork borer and spatula after use.

Almost fill the well in the agar with the diluted penicillin solution.

11 Cover the plate and seal using small pieces of adhesive tape, as shown in Figure 2. *Do not totally seal round the rim* as this may create anaerobic conditions and encourage the growth of harmful bacteria.

Label the plate with your initials, the name of the micro-organism and the date. Write something to indicate the treatment given to the plate. (**Do not lick the labels**.)

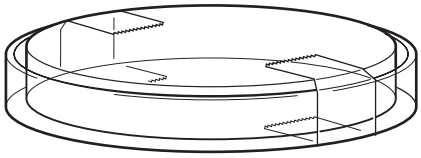


Figure 2

12 Now set up three control plates in the same way, to compare with your penicillin sample. Fill the well in the agar of the first plate with 6-APA solution, and the well in the second plate with sodium benzoate solution: you are provided with these two solutions. (Their concentrations have been adjusted to about $50\,\mu g\,cm^{-3}$, comparable to that of the penicillin solution). Leave the well in the third plate empty. Cover, seal and label the plates as before.

13 Take care not to tip the plates. Leave them on the bench at room temperature (20 °C) for 24–48 hours. Do not leave them where other people can interfere with them (a secure corner of the prep room is probably best).

14 Make sketches of the four plates at the end of this time. (**CARE** Do not open the plates once they have been sealed.) The agar will appear cloudy in the areas where bacteria are growing. (You will see this more clearly if you hold the plates up to the light.)

Using a ruler, measure the size of any inhibition of bacterial growth. Did your penicillin solution show any antibacterial activity?

CARE Any material which has come into contact with the bacterial culture must be sterilised before disposal, or before returning to stock cupboards. The sealed plates must be sterilised in a pressure cooker or an autoclave before disposal.

QUESTIONS

a Explain why the penicillin you made is called a *semi-synthetic* penicillin.

b Why was NaOH(aq) added to the 6-APA in step **2**, before treatment with benzoyl chloride?

c What product other than penicillin is formed when 6-APA reacts with benzoyl chloride? What *type* of bond is formed in this reaction?

d Explain how the penicillin you produced was purified.

e Why was it necessary to have the three control plates when testing for antibacterial activity?

MD5.2

A closer look at the structure of penicillins (*Optional extension*)

In this activity you will make a model of the 'penicillin nucleus', 6-APA, and investigate its stereochemistry. You will then investigate the effect of the structure of the side-chain on the antibacterial activity of different penicillins.

Requirements

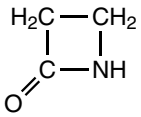
- set of molecular models
- molecular modelling software (optional)

What you do

Work in small groups to carry out this activity. This will speed up the model-building, and allow you to discuss the answers to the questions while you are looking at the models.

Part 1: Modelling penicillins

1 Start by making a model of a simple β-lactam ring:



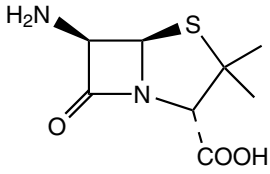
β-lactam ring

a What functional group is present in the β-lactam ring?

b Suggest why the β-lactam ring is so susceptible to attack by acids and alkalis, and reacts readily to form open-chain compounds.

2 Now convert your β-lactam model into a model of 6-amino penicillanic acid (6-APA). This is the 'pencillin nucleus' common to all penicillins.

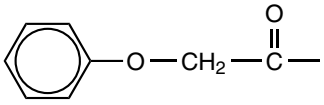
Before you do this, look at the formula of 6-APA very carefully. The molecule has a very precise stereochemistry:



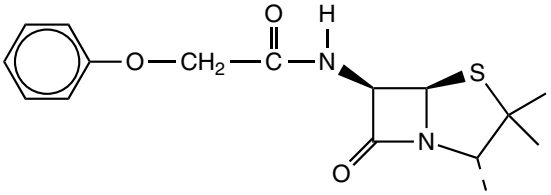
6-APA

c How many chiral carbon atoms are there in a molecule of 6-APA? Mark these on the diagram with an asterisk (*).

3 If your model kit is large enough, you could add an acyl group, and convert your model of 6-APA into a model of a penicillin. For example, substituting



for an H atom in the $-NH_2$ group converts 6-APA into penicillin V.



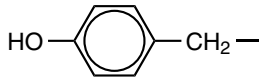
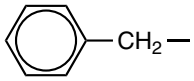
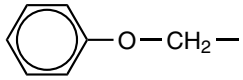
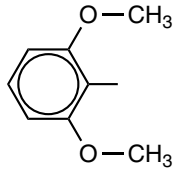
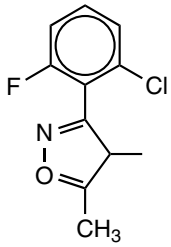
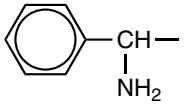
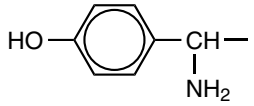
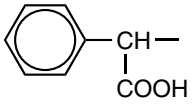
penicillin V

d The other optical isomers of penicillin V are much less active against bacteria. Explain why the correct stereochemistry is crucial.

e The structure of penicillin V was worked out in the 1940s, but it was not synthesised chemically until 15 years later. Why do you think totally synthetic penicillins have never been produced commercially on a large scale?

Part 2: Looking at the side-chain (R—CO—)

The table below shows the R groups in the side-chains of some natural penicillins and some semi-synthetic ones, together with some information about their main uses.

Name	R group in the side-chain	Natural/ semi-synthetic	Uses/properties
Penicillin F	$CH_3CH_2CH{=}CHCH_2-$	natural	not used commercially
Penicillin X		natural	not used commercially
Penicillin K	$CH_3(CH_2)_6-$	natural	not used commercially
Penicillin G		natural	general infections, gonorrhoea and syphilis
Penicillin V		natural and semi-synthetic	general infections, ear, nose and throat
Methicillin		semi-synthetic	controlling resistant *Staphylococcus*
Flucloxacillin		semi-synthetic	controlling resistant *Staphylococcus*
Ampicillin		semi-synthetic	lung and wound infections
Amoxycillin		semi-synthetic	lung and urinary tract infections
Carbenicillin		semi-synthetic	pneumonia, burns

f Explain the distinction between natural and semi-synthetic penicillins.

g **i** Look at the R group in the side-chains of methicillin and flucloxacillin. What structural feature of penicillins appears to be important in resisting attack by the β-lactamase enzyme?
(**Hint** Look at the groups attached to the first carbon in the side-chain. Remember that large groups affect the size and shape of a molecule.)

ii Suggest how penicillins such as methicillin and flucloxacillin are able to resist attack by the β-lactamase enzyme.

iii Penicillins act by inhibiting a bacterial enzyme that helps to make the bacterial cell wall. How might the active site of this enzyme differ from the active site of β-lactamase?

MD6

Check your notes on *Medicines by Design*

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.

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 chemical principles behind methods which can be used to detect ethanol in the body (g.l.c. and i.r. spectroscopy) (**Storyline MD1**; **Activity MD1.2**).
- The following reactions involving aldehydes and ketones: formation by oxidation of alcohols, oxidation to carboxylic acids, reduction to alcohols and reaction with hydrogen cyanide (**Activity MD1.1**).
- The mechanism of the nucleophilic addition reaction between an aldehyde or a ketone and hydrogen cyanide.
- The meaning of the terms: *drug, medicine, molecular recognition, pharmacological activity, pharmacophore, receptor site, agonist, antagonist, lead compound* (**Storyline** in general).
- The structure of a pharmacologically active material in terms of its functional components: pharmacophore and groups which modify the pharmacophore (**Storyline MD3**).
- The action of biologically active chemicals and how this relates to their interaction with receptor sites.
- The factors affecting the way that species interact in three dimensions: size, shape, bond formation and orientation (**Storyline MD4**).
- The role of chemists in designing and making new compounds for use as pharmaceuticals (**Storyline MD3**, **MD4** and **MD5**).
- The role of computer modelling techniques in the design of medicines (**Storyline MD4**).
- The identification of functional groups within a polyfunctional molecule, as a way of making predictions about its properties.
- How to devise synthetic routes for preparing organic compounds.
- The use of the following terms to classify organic reactions: *hydrolysis*, *oxidation*, *reduction*, *condensation* and *elimination*.
- The classification of organic reactions according to their reaction mechanisms: nucleophilic substitution, electrophilic addition, electrophilic substitution, nucleophilic addition and radical.
- The use of a combination of spectroscopic techniques (m.s., i.r., n.m.r. and u.v. and visible) to elucidate the structure of organic molecules.

Pulling together organic chemistry

1. Make sure you are familiar with the organic functional groups you have met throughout the course. It may help to draw up a table giving the name and formula of each functional group, and an example of a simple molecule containing the group.
2. Make sure you are familiar with the main reactions of each functional group. You should be able to write an equation and give essential conditions for each reaction.
3. Practise using the toolkit in **Activities MD3.1**, **MD3.2** and **MD3.3** as much as you can. You must be able to use the reactions you have learned in this course, together with any further ones you may be given, to devise synthetic routes for preparing organic compounds.