Salters Advanced Chemistry
Module 2 Activities Booklet

Chemistry of Natural Resources

2848

AS

M From Minerals to Elements
A The Atmosphere
PR The Polymer Revolution

A2 (2849)

WM What's in a Medicine?

Chemistry of Natural Resources

Module 2 – 2848 - Activities Booklet

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MI.I

Solutions of ions

This activity uses simple test-tube experiments to illustrate the properties of ionic solutions.

Requirements

- test-tubes
- teat pipettes
- 10 cm^3 measuring cylinder
- copper(II) carbonate, solid (1 spatula measure)
- copper(II) sulphate solution, 1 mol dm^{-3} (6 cm^3)
- sodium nitrate(V) solution, 1 mol dm^{-3} (10 cm^3)
- sodium carbonate solution, 1 mol dm^{-3} (2 cm^3)
- lead nitrate(V) solution, 1 mol dm^{-3} (3 cm^3)
- potassium iodide solution, 1 mol dm^{-3} (1 cm^3)
- hydrochloric acid, 1 mol dm^{-3} (3 cm^3)
- sodium hydroxide solution, 1 mol dm^{-3} (2 cm^3)
- sulphuric acid, 1 mol dm^{-3} (2 cm^3)
- sodium chloride solution, 1 mol dm^{-3} (1 cm^3)

copper(II) carbonate

copper(II) sulphate solution

lead nitrate(V) solution

dilute sodium hydroxide solution

dilute sulphuric acid

CARE Eye protection must be worn.

If you had a crystal of copper(II) sulphate which was large enough to test its electrical conductivity, you would find that it does not conduct. But if you dissolve copper(II) sulphate crystals in water, the resulting solution does conduct electricity. These simple observations provide some direct evidence to support the theory about what happens when an ionic compound such as copper(II) sulphate dissolves in water:

- Solid ionic compounds consist of regular giant ionic lattices, with the positive and negative ions in fixed positions. The ions cannot move and so the solid does not conduct electricity.
- When an ionic compound dissolves in water, the ions separate and become surrounded by water molecules (hydrated). The ions move about independently in the solution and so the solution conducts electricity.

You will find all of the small tests that you do in this activity easy to explain if you remember to picture any solution of an ionic compound as consisting of positive and negative ions moving independently throughout the solution. You also need to know that all sodium and potassium salts are soluble at the concentrations used in these tests.

What you do

Using Table 1, carry out the tests as instructed below. In the observation column of the table record *what you see*, not what you think is happening. But keep thinking about what is happening. You need to be clear about the ions present in each compound. It may help to write the name of each compound below the formula in the table.

After answering each set of questions, write an explanation of your observations in the last column of the table, using at least two words from this list for each experiment:

mixing
diluting
dissolving
precipitating
solution
insoluble salt
soluble salt
acid-base

The first row of the table has been filled in as an example.

1 Carry out experiments **i** to **iv** by mixing the reagents shown in Table 1.

a What is the concentration of $Cu^{2+}(aq)$ ions in a 1 mol dm^3 solution of copper(II) sulphate?

b What is the concentration of $SO_4^{2-}(aq)$ ions in a 1 mol dm^{-3} solution of copper(II) sulphate?

c What is the concentration of each of $Cu^{2+}(aq)$ and $Cl^-(aq)$ ions in a 1 mol dm^{-3} solution of copper(II) chloride, $CuCl_2(aq)$?

2 Carry out experiments **v** to **ix**.

d What would you expect to see if you mixed the lead nitrate(V) solution with sodium chloride solution, instead of hydrochloric acid, in **ix**? Carry out the mixing to check your prediction.

3 Carry out experiments **x** to **xii**.

e The enthalpy change when
1 dm^3 of 1 mol dm^{-3} NaOH(aq) reacts with
1 dm^3 of 1 mol dm^{-3} HCl(aq)
is the same as the enthalpy change when
1 dm^3 of 1 mol dm^{-3} NaOH(aq) reacts with
1 dm^3 of 1 mol dm^{-3} solution of $HNO_3(aq)$.
How does this evidence support the theory that these three substances exist as separate ions when in dilute aqueous solution?

4 When you have completed the explanation column of Table 1, write full equations, with state symbols, for each chemical reaction that occurred in the tests you carried out. Then write ionic equations for each of these reactions.

Reagents	Observations	Explanation
i 1 cm^3 $CuSO_4(aq)$ + 5 cm^3 H_2O	Blue solution becomes paler as water is added	Words used: diluting, mixing, solution
ii 5 drops $CuSO_4(aq)$ + 5 cm^3 H_2O		
iii 1 cm^3 $CuSO_4(aq)$ + 5 cm^3 $NaNO_3(aq)$		
iv 5 drops $CuSO_4(aq)$ + 5 cm^3 $NaNO_3(aq)$		
v 1 cm^3 $CuSO_4(aq)$ + 1 cm^3 $Na_2CO_3(aq)$		
vi 1 cm^3 $CuSO_4(aq)$ + 1 cm^3 $NaOH(aq)$		
vii 1 cm^3 $CuSO_4(aq)$ + 1 cm^3 $Pb(NO_3)_2(aq)$		
viii 1 cm^3 $Pb(NO_3)_2(aq)$ + 1 cm^3 $KI(aq)$		
ix 1 cm^3 $Pb(NO_3)_2(aq)$ + 1 cm^3 $HCl(aq)$		
x 1 cm^3 $Na_2CO_3(aq)$ + 2 cm^3 $HCl(aq)$		
xi 1 cm^3 $NaOH(aq)$ + 1 cm^3 $HCl(aq)$		
xii 1/2 spatula $CuCO_3(s)$ + 2 cm^3 $H_2SO_4(aq)$		

Table 1 Results table

MI.2

Bromine production

This activity is designed to help you to understand the role of redox reactions in the production of bromine.

The flow diagram in Figure 1 describes the production of bromine from water from the Irish Sea. It provides a simplified diagrammatic summary of the sequence of steps in the process and identifies the inputs and outputs of each step. This flow diagram does not provide any information about the energy transfers in the process.

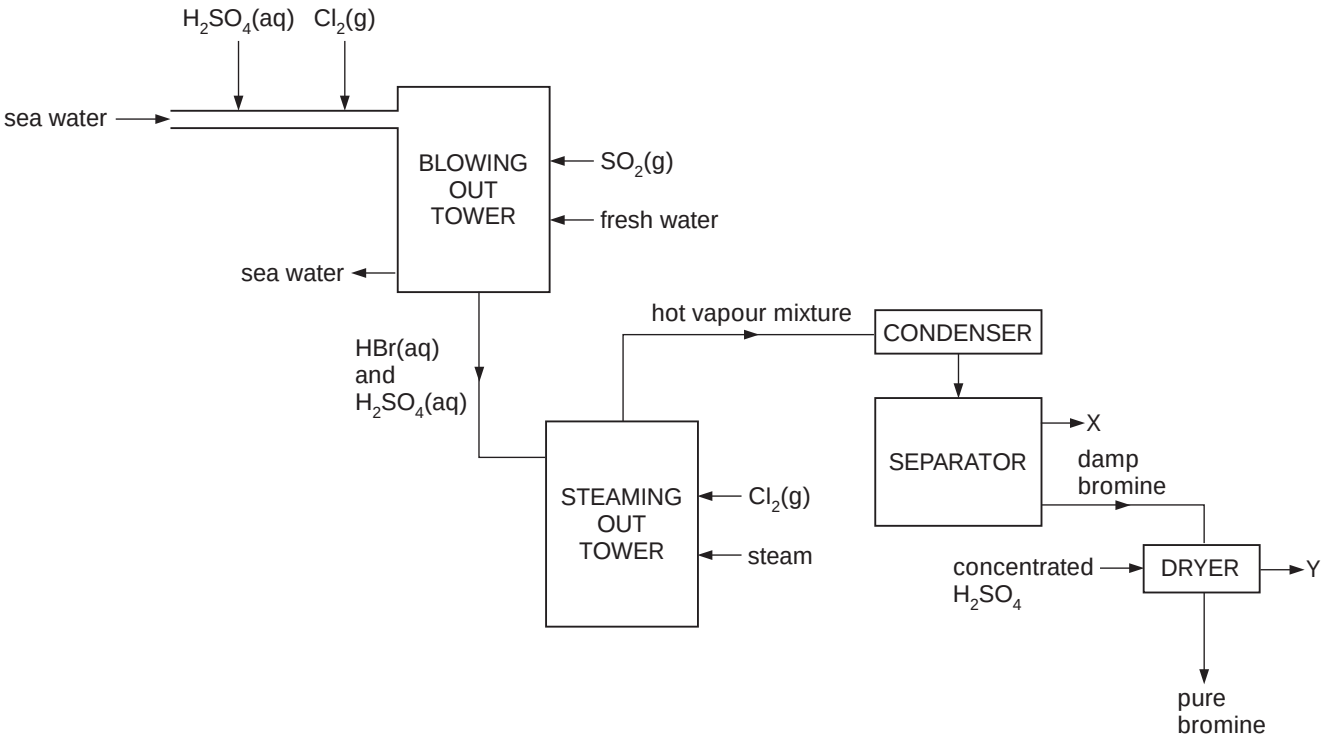


Figure 1 Flow diagram for bromine production at the Almwch works

QUESTIONS

a Write an equation, with state symbols, for the redox reaction occurring in:
- **i** the sea water inlet pipe
- **ii** the blowing-out tower
- **iii** the steaming-out tower.

For each reaction identify what is oxidised and what is the oxidising agent.

b Which of the properties of bromine make it possible to separate it from water?

c What would you expect the *hot vapour mixture* leaving the steaming-out tower to contain?

d Suggest what the outputs would be at points *X* and *Y*.

e Identify a point on the flow diagram where:
- **i** heating is required
- **ii** cooling is required.

MI.3

Halogens and their compounds

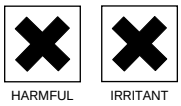
In this activity you are going to find out about some of the properties of the elements chlorine, bromine and iodine, and their compounds. You need to be able to recognise the elements when pure and when in solution. Their appearances will help you to work out what is happening during your investigations. These experiments will help you learn some factual chemistry, and will give you practice at observing and interpreting chemical changes.

Requirements

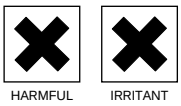
- chlorine solution, in water (5 cm^3)
- bromine solution, in water (5 cm^3)
- iodine solution, in water (5 cm^3)
- test-tubes
- rubber bungs
- potassium chloride, solid (2 g)
- potassium bromide, solid (2 g)
- potassium iodide, solid (2 g)
- potassium chloride solution, 0.1 mol dm^{-3} (10 cm^3)
- potassium bromide solution, 0.1 mol dm^{-3} (10 cm^3)
- potassium iodide solution, 0.1 mol dm^{-3} (10 cm^3)
- silver nitrate solution, 0.025 mol dm^{-3} (1 cm^3)
- cyclohexane (30 cm^3)

CARE Cyclohexane is highly flammable. Return residues containing cyclohexane to a residues bottle. Do not pour them down the sink.

bromine solution



chlorine solution



cyclohexane

iodine solution

CARE Eye protection must be worn.

Appearances and solubilities of halogen elements

1 Draw up a table like the one below so that you can record the following information for chlorine, bromine and iodine:

- state and colour at room temperature
- colour of vapour
- colour of aqueous solution
- colour of solution in cyclohexane
- relative solubility in water and cyclohexane.

Use a textbook if necessary to find out about the appearances of the halogens.

	Chlorine	Bromine	Iodine
state and colour at room temperature			

2 Observe the behaviour of the halogens in water and in cyclohexane by taking a few cm^3 of a halogen solution in water in a test-tube. Then stopper the tube and shake the solution with an equal volume of cyclohexane. (**CARE** Chlorine and bromine solutions have harmful vapours. Avoid breathing the fumes from the solutions.) Add this information to your table.

Appearances and solubilities of halogen compounds

3 Draw up a table like the one on the next sheet and record the following points about potassium chloride, potassium bromide and potassium iodide:

- state and colour at room temperature
- solubility in water
- colour of aqueous solution
- solubility in cyclohexane.

The properties of the potassium halides are typical of the alkali metal halides in general.

You can either look up the solubilities of the salts in a databook or investigate them for yourself. Use the key shown in Figure 1 to help you decide what the relative solubilities are. A suitable volume of solvent to use for these experiments is about 3 cm^3.

	Potassium chloride	Potassium bromide	Potassium iodide
state and colour			

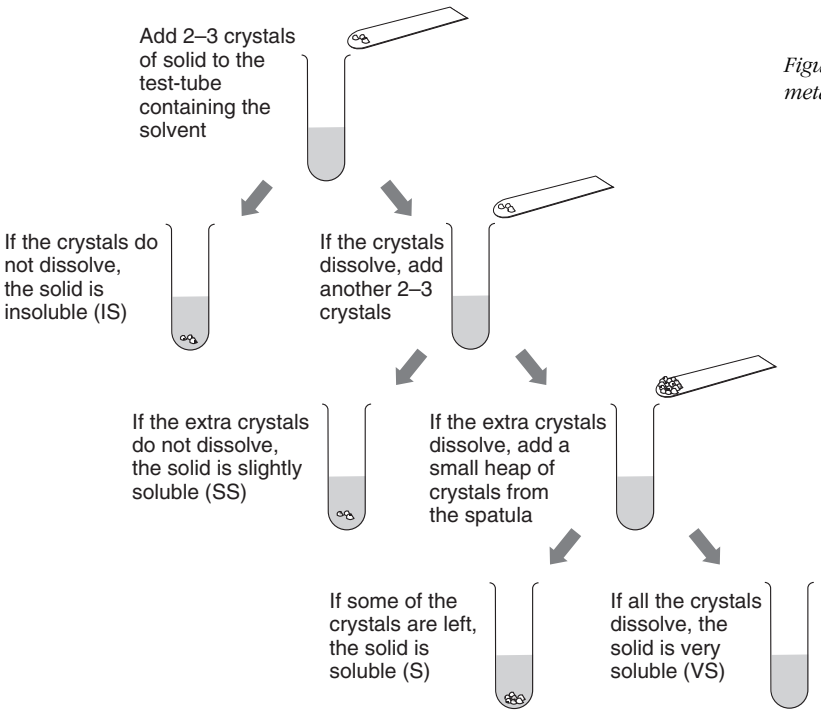


Figure 1 Key for investigating solubilities of alkali metal halides

QUESTIONS

a What general patterns are there in the appearance, volatility and solubility of the halogens? Make a note of your conclusions. Predict the properties you would expect for the other two halogens – fluorine and astatine.

b What general pattern can you find in the solubilities of the alkali metal halides? Make a note of your conclusions. Predict the solubilities in water and cyclohexane of potassium fluoride and potassium astatide.

Displacement reactions of halogens

4 Add a few drops of aqueous chlorine solution to aqueous potassium bromide in a test-tube. Observe what happens. It may help you interpret what happens if you observe the effect of shaking the reaction mixture with an equal volume of cyclohexane.

5 Now try other combinations of solutions of halogen elements with solutions of halide salts and look for a pattern. Record your observations and interpretations in a table like the one shown below:

Halogen added	Observation/ interpretation	Potassium chloride solution	Potassium bromide solution	Potassium iodide solution
chlorine	appearance of aqueous solution			
	appearance of cyclohexane solution			
	names of products			

Reactions of halide ions with silver nitrate solution

6 Add 2 cm^3 of one of the potassium halide solutions to a test tube and then add a few drops of silver nitrate solution. (**CARE** Silver nitrate stains your skin and clothes if spilled.) Observe what happens.

Repeat the process with solutions of the other two potassium halides.

7 Place the tubes and contents in daylight near a window. Observe what happens to the contents over a period of about half an hour.

Record your observations and interpretations in a table like the one shown below.

Halide ion	Effect of adding silver nitrate		Effect of light	
	Observation	Interpretation	Observation	Interpretation
chloride ion				

QUESTIONS

c i Write ionic equations for the reactions of:
- chlorine with bromide ions
- bromine with iodide ions.

ii Explain how these reactions can be classified as redox reactions.

d i What order for the relative oxidising powers of the halogens is suggested by your results for the displacement reactions?

ii Suggest positions for fluorine and astatine in relation to the other halogens in your list for **d i**.

iii What general pattern emerges from the displacement reactions?

e There is a pattern to the appearances of the silver halides. Explain what it is.

f i Is there a pattern in the photosensitivities of the silver halides? Explain your answer.

ii Interpret the effect of light on the silver halides in terms of ideas about redox.

g Silver halides are used in photography. Which silver halide would be most useful in:

i *fast* photographic film – film which can be used in low light levels?

ii X-ray film, which is exposed to very high light energies?

h Iodine undergoes a redox reaction with thiosulphate ions, $S_2O_3^{2-}(aq)$. The reaction is often used in analysis. The products are iodide ions, $I^-(aq)$, and tetrathionate ions, $S_4O_6^{2-}(aq)$.

i State the oxidation number of sulphur in:
- $S_2O_3^{2-}$
- $S_4O_6^{2-}$.

ii Write a balanced equation for the reaction of iodine with thiosulphate ions.

iii Explain why this can be regarded as a redox reaction.

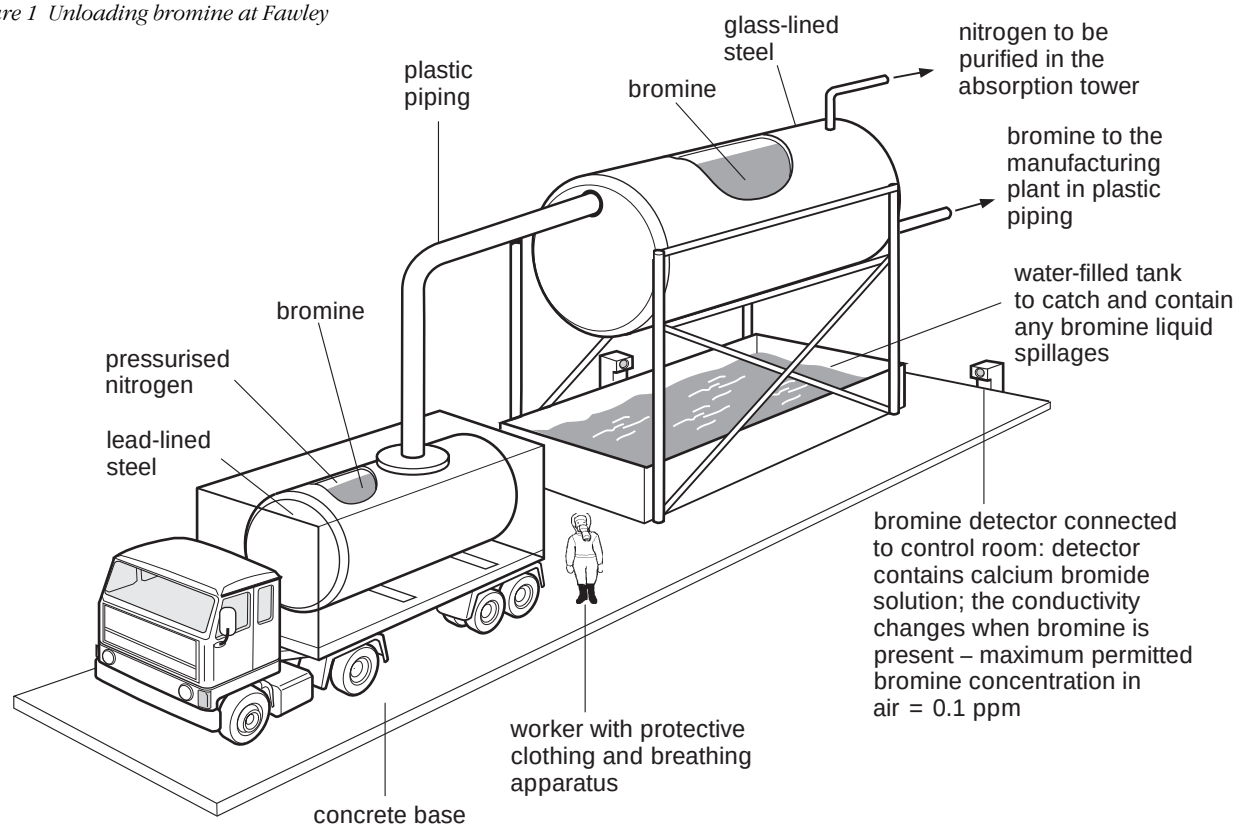
MI.4

This liquid is dangerous

This activity looks at how a hazardous chemical like bromine is handled on a large scale. To answer the questions you will need to think about how choice of construction materials and safety considerations are related to the design of the equipment which is used.

Imagine what it must be like to be the person who is responsible for unloading tankers full of bromine. Figure 1 shows the part of the plant at Fawley, near Southampton, where bromine is transferred from road tankers to be used in the manufacture of bromobutyl rubber. It should help you answer some of the questions which follow.

Figure 1 Unloading bromine at Fawley



a **i** What properties of glass make it suitable for lining the bromine storage tank?

ii Why do you suppose that lead is preferred for lining the lorry tanks?

b Imagine that you are drawing up safety rules for the plant. What instructions would you give for dealing with small leaks of liquid bromine? What chemical method would you choose to get rid of the spilt liquid? (You may need to refer to a textbook to answer this question.)

Questions **c**–**g** are about the absorption tower which is used to remove bromine vapour from the nitrogen before it is released into the atmosphere. The absorption tower is not shown on the diagram; it is described below.

Unlike most of the pipes and towers in a petrochemicals plant, the bromine absorption tower is made of glass so that it is possible to see what is happening inside. It is packed with short lengths of glass tubing and contains a concentrated aqueous solution of sodium hydroxide. Waste gases, including bromine vapour, enter roughly in the middle of the absorption tower, so the glass packing extends above and below the point at which the gases enter.

Sodium hydroxide reacts with bromine according to the equation:

$$2NaOH(aq) + Br_2(g) \rightarrow NaBr(aq) + NaOBr(aq) + H_2O(l)$$

The sodium hydroxide solution is strongly alkaline, whereas the solution produced from the reaction is only weakly alkaline. The sodium hydroxide is circulated by a pump, and a flow meter checks that the pump is working.

A pH meter is one of the other detectors used to monitor the efficiency of the absorption tower.

c What change would you expect to see in the bromine vapour after it has entered the absorption tower?

d Suggest reasons why the tower is packed with glass tubing, and why the column is packed below the point where nitrogen enters the tower.

e Explain why sodium hydroxide solution is suitable for absorbing bromine.

f Suggest why a pH meter is included as part of the absorption tower's monitoring equipment.

g Draw a sketch of how you would design an absorption tower based on the description given above. Label your sketch to indicate the chemicals, reactions, etc., where appropriate.

MI.5

Manufacturing chlorine

The purpose of this activity is to provide you with a description of modern chlorine manufacture. When you have finished, you should be able to describe the chemistry involved in the manufacture of chlorine, and you should be aware of the technology used to apply this chemistry efficiently.

The electrolysis of brine

Chlorine is a vital commodity for the chemical industry. One of its uses is to produce bromine from sea water.

Chlorine can be made by electrolysis of a concentrated solution of sodium chloride (sometimes called *brine*). The other products are hydrogen and the alkali, sodium hydroxide (often called *caustic soda* in the industry).

Chlorine manufacture and sodium hydroxide manufacture are directly linked, so we often talk about the *chlor-alkali industry*. In the UK this is based mainly on the underground salt deposits in Cheshire. One problem for the chlor-alkali industry is to ensure that demand for all three of its products is kept in line with the production rate.

There are two well-established technologies for electrolysing brine: the *mercury cell* and the *diaphragm cell*. A third is a more modern cell, the *membrane cell*, which has only been used since the early 1980s. As the membrane cell is the fastest growing technology for the manufacture of chlorine it has been chosen for this discussion.

a The half-equations involved in the electrolysis of sodium chloride solution are:

at the positive electrode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
at the negative electrode: $2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)$

These two gases are evolved, chlorine at the positive electrode and hydrogen at the negative electrode.

i In each case state whether the half-reaction corresponds to reduction or to oxidation.

ii Sodium ions and hydroxide ions are left in the solution. What is likely to be the impurity in this solution of sodium hydroxide?

b **i** Calculate the amount (in moles) of sodium hydroxide, NaOH, in one tonne of solid sodium hydroxide.

ii What amount (in moles) of chlorine, Cl_2, is produced for each mole of NaOH?

iii Calculate the mass of chlorine produced at the same time as one tonne of sodium hydroxide.

c Use a reference book (such as *The Essential Chemical Industry*, available from the Chemical Industry Education Centre at the University of York) to find information about the uses of chlorine, sodium hydroxide and hydrogen. Display the information in the form of pie-charts. If you have access to a graphics package on a computer, use this to draw your pie-charts.

Cell design

Any electrolysis cell used to make chlorine, hydrogen and sodium hydroxide by the electrolysis of sodium chloride solution must be designed to:

- prevent chlorine produced at the positive electrode reacting with the hydroxide ions around the negative electrode
- minimise chloride ions diffusing into the solution around the negative electrode which would contaminate the sodium hydroxide solution
- minimise hydroxide ions being lost by diffusion away from the negative electrode towards the positive electrode
- prevent mixing of chlorine and hydrogen which could lead to an explosion.

Membrane cell

The electrolysis cell (Figure 1) uses a membrane which acts as a barrier to all gas and liquid flows and allows only the transport of charged sodium ions between compartments. Sodium ions pass through in hydrated form $(Na.xH_2O)^+$, so some water is transferred, but the membrane is impermeable to free water molecules.

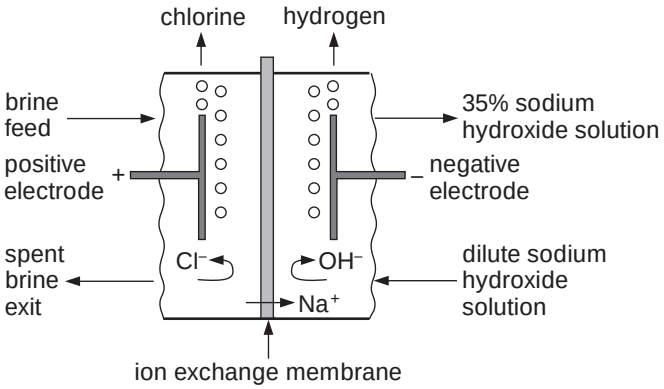


Figure 1 The membrane cell for the manufacture of chlorine, hydrogen and sodium hydroxide

The commercial use of this type of cell was not possible until work by Du Pont in the US in the early 1970s, and more recently in Japan, resulted in the production of a satisfactory material to act as a membrane.

The specification for the cell membrane is very demanding. It must be:

- permeable to $Na^+(aq)$ ions
- impermeable to $Cl^-(aq)$ and $OH^-(aq)$ ions
- resistant to chlorine and sodium hydroxide solution that is almost 9 mol dm^{-3}
- stable at about 90 °C – the temperature of the solution in the electrolysis cell.

The membranes are based on *poly(tetrafluoroethene)*, usually referred to as *ptfe* or *Teflon*, which is resistant to high temperatures and to chemical attack. (One of the other uses of ptfe is as the non-stick coating on pans.) The electrolysis membranes are usually about 0.2 mm thick. Each cell contains 60 sheets of membrane, each with an area of 0.21 m^2.

The ptfe is modified for use in membranes by building onto it some negatively-charged side-chains, carboxylate ($–COO^-$) and sulphonate ($–SO_3^-$). These attract the positive sodium ions but repel negative ions like $OH^-(aq)$. The $Na^+(aq)$ ions pass through the membrane, pulled by the charge on the negative electrode (Figure 2).

Membranes have been developed which allow cells to operate at potential differences as low as 3 V, and with resistances low enough to allow the use of currents of about 4000 A m^{-2}. The electrical heating effect of a current of this size keeps the electrolysis solution hot.

d Explain why the membrane needs to be:
  i permeable to $Na^+(aq)$ ions
  ii impermeable to $Cl^-(aq)$ and $OH^-(aq)$ ions.

e Before it is used, the brine must be carefully purified to remove $Ca^{2+}(aq)$ and $Mg^{2+}(aq)$ ions.

Suggest why this is necessary.

f Describe how well the membrane cell meets the ideal cell design criteria listed earlier.

g The membrane cell is preferred these days to the other two types of cell. Even so, the bulk of chlorine production in the UK is from mercury cells.

Suggest one reason:
  i why the membrane cell may be preferred
  ii why the mercury cells have not been replaced by membrane cells.

h Electrolysis is also used to make sodium metal from sodium chloride. Suggest how this process will need to be different from that used to manufacture hydrogen, sodium hydroxide and chlorine.

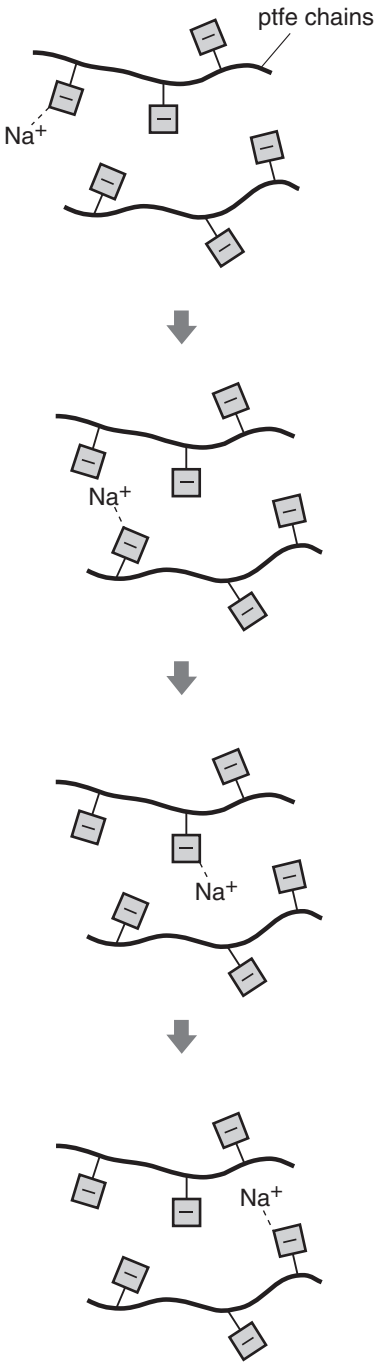


Figure 2 Sodium ions passing through a channel in an electrolysis cell membrane

M2.1

Mineral spotting

You are provided with a sample of rock which has been taken from a mineral lode in the Pennines. The sample has been ground to a powder to liberate the grains of the minerals that are present. In this activity you will look for evidence of hydrothermally deposited minerals. In a later activity you will use a similar sample which has been roasted, and extract some copper from it.

Requirements

- unroasted sample of copper ore (2 g)
- boiling tube
- microscope slide
- microscope with table lamp to illuminate sample from above
- spatula
- samples of chalcopyrite, galena, sphalerite, quartz, fluorite, calcite, malachite

What you do

1 Shake about 2 g of unroasted ore in a boiling tube about one-third full of water.

2 Leave the tube until the larger particles of solid have settled to the bottom but the smaller particles are still in suspension, then decant away the dirty water.

3 Spread out some of the damp sediment from the bottom of the tube on a microscope slide. Examine the grains of sediment under a microscope using illumination from the top. Use the lowest power of magnification on the microscope and try to identify as many minerals as possible from the list at the end of the activity. If you have access to larger samples of minerals, examine samples of the minerals you have identified under the microscope.

QUESTIONS

a Which minerals are present in your sample of copper ore?

b Has the process of liberation been effective? Have the mineral grains been set free from the host rock?

c Approximately what size are the mineral grains in your sample? (Use a ruler or something similar to make an estimate.)

Data: some hydrothermal minerals

Mineral	Appearance*
chalcopyrite, $CuFeS_2$	brassy yellow; metallic-looking
bornite, Cu_5FeS_4	red/brown with streaks of blue
malachite, $Cu_2(OH)_2CO_3$	green; dull-stony looking
azurite, $Cu_3(OH)_2(CO_3)_2$	deep blue
galena, PbS	blue-grey; metallic-looking
sphalerite, ZnS	black-brown; metallic-looking
quartz, SiO_2	white-colourless; glassy-looking, irregular shape
calcite, $CaCO_3$	white-colourless; sometimes with streaks of colours
fluorite, CaF_2	colour very variable, for example, pale yellow, pale blue; cubic shape

*The minerals have many different appearances. The data given here describe some of the colours in which they occur.

M2.2

Getting at the minerals

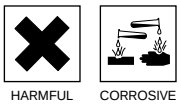
***Roasting is a process which converts sulphide minerals into oxides. In this activity, a sample of ore containing copper sulphide has been roasted to produce copper oxide. You are going to investigate two methods of dissolving the copper compounds out of the roasted ore: (1) using acid, (2) using ammonia. Afterwards you should be able to explain why the ammonia method is used for* Activity M2.3.**

Requirements

- 100 cm^3 beakers
- clingfilm or watch-glasses
- 10 cm^3 measuring cylinder
- sample of roasted copper ore (6 g)
- hydrochloric acid, 50% (10 cm^3)
- ammonia leach solution
  – 192 g ammonium carbonate dissolved in 1 dm^3 of 4 mol dm^{-3} ammonia solution (10 cm^3)
- domestic food-warming tray to use as a heating mat

CARE The leach solution produces an irritating vapour. Avoid inhaling the fumes. Use the solution in a fume cupboard.

ammonia solution



hydrochloric acid

CARE Eye protection must be worn.

What you do

1 Put about 3 g of the roasted ore into each of two beakers. Add 10 cm^3 of the hydrochloric acid (**CARE** Corrosive) to one beaker and cover it loosely with clingfilm or with a watch-glass.

2 Add 10 cm^3 of the ammonia leach solution (**CARE** Corrosive; harmful vapour) to the other beaker. Cover this beaker in the same way.

3 After the initial reaction has subsided, warm both beakers for 10 minutes on the domestic food-warming tray.

QUESTIONS

a What changes occurred in the two beakers? Explain what happened.

b Explain why using the ammonia leach provides the better way of extracting the copper.

M2.3

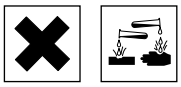
Extracting copper

In this activity, copper compounds are dissolved out of a roasted ore sample using an ammonia leach solution. The copper is then separated by displacing it from solution with zinc. The activity gives you an idea of the quantities of waste and useful mineral in an ore sample, and introduces you to some of the processes used at Bingham Canyon.

Requirements

- roasted copper ore (50 g)
- 250 cm^3 conical flask
- cottonwool
- ammonia leach solution – see **Activity M2.2** (100 cm^3)
- 100 cm^3 measuring cylinder
- domestic food-warming tray to use as a heating mat
- test-tubes
- apparatus for vacuum filtration (if available)
- 400 cm^3 beaker
- 250 cm^3 beaker
- sulphuric acid, 4 mol dm^{-3} (40 cm^3)
- sodium hydroxide solution, 2 mol dm^{-3} (access to reagent bottle)
- Universal Indicator paper
- zinc dust (4 g)
- propanone (20 cm^3)
- watch-glass
- glass rod
- access to balance
- access to fume cupboard
- filter funnels

ammonia solution



propanone

sodium hydroxide solution

sulphuric acid

CARE Eye protection must be worn.

CARE The leach solution has a toxic vapour. Use a fume cupboard when instructed to do so.

Additional requirements (optional)

- 250 cm^3 volumetric flask
- 10.0 cm^3 pipette
- pipette filler
- 100 cm^3 conical flask
- burette
- ammonium ethanoate, solid (10 g)
- potassium iodide, solid (5 g)
- sodium thiosulphate solution, 0.100 mol dm^{-3} (50 cm^3)
- freshly made starch solution (5 cm^3)

Flow diagram

This activity is quite long and involved. It might help you to follow the process more clearly if you regard it as built up from the four stages which are indicated in the flow diagram (Figure 1).

Figure 1

Steps 1 & 2
Ore reacts with leach solution.
Mixture is washed with water.

→

Steps 3–7
Filtering off solution of leached copper.
Washing to remove further traces of leached copper.

→

Steps 8–9
Neutralisation of leached solution.
(**Optional E1–E9** Analysis of Cu^{2+} ions in leached solution.)

→

Steps 10–15
Displacement of copper from solution using zinc.
Removal of excess zinc and collection of pure copper.

Leaching the ore

1 Place about 50 g roasted ore in a 250 cm^3 conical flask. Add 100 cm^3 of the ammonia leach solution which you used in **Activity M2.2**. (**CARE** Toxic vapour. Do this part of the activity in a fume cupboard.) Gently swirl the mixture. Fit a cottonwool plug loosely into the neck of the flask and place it on the food-warming tray, in a fume cupboard, for between 30 minutes and an hour.

2 Add 20 cm^3 of water, swirl the flask and contents once more, then leave them to stand overnight in the fume cupboard, which should be left on if ammonia gas is still being released.

During this first stage of the extraction, Cu^{2+} ions in the roasted ore dissolve into the leach solution.

a Leaching is most effective when warm solution is left in contact with the ore for a long time. Explain why this is so.
b Explain why there is a limit to the time a mining company can spend on leaching.

Vacuum filtration

3 Carefully pour off the leach solution from the solid which has settled to the bottom of the conical flask. (**CARE** Toxic vapour. Do this part of the activity in a fume cupboard.) Disturb the solid as little as possible. Add 40 cm^3 of water to the solid left over in the flask, swirl them together and leave them to settle while you filter the decanted leach solution.

4 Assemble a vacuum filtration apparatus like the one shown in Figure 2. There are many variations on the equipment used – your teacher may need to show you a different assembly. Use a 250 cm^3 conical flask and a coarse filter paper.

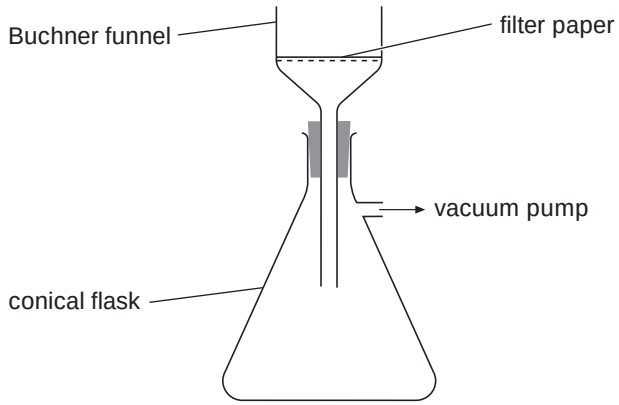


Figure 2 Diagram of a vacuum filtration assembly

Vacuum filtration is normally used to separate mixtures when the solid is required and the solution is waste. Ordinary filtration is used when you want a pure solution. In this activity it is actually the *filtrate* you want to collect, but the solid contains some very fine particles which clog up the filter paper and make ordinary filtration very slow. If available, vacuum filtration separates the solution more quickly, but it is less efficient. Do not worry if your solution is contaminated with a little solid: you will filter it properly at a later stage.

5 Filter the decanted leach solution, then transfer the filtrate to a 400 cm^3 beaker.

6 When the liquid from the first washing of the solid is fairly clear, decant this too and filter it using a new filter paper. Notice the colour of the filtrate and add it to the other filtrate in the 400 cm^3 beaker.

7 Add a second 40 cm^3 portion of water to the solid. Shake them together and leave them to separate. Decant the liquid and filter it using a new filter paper. Notice the colour of the filtrate and combine it with the other filtrates.

c **i** What were the colours of the three filtrates?
ii Do you think you managed to extract all the leached copper into your 400 cm^3 beaker? Explain your answer.
iii Why is it not worth continuing to wash the ore with further quantities of water?
iv How could you recover the ammonia from the filtrate for re-use in step **1**?

Neutralising the leached solution

The combined filtrate contains copper(II) ions in addition to hydroxide ions, carbonate ions and ammonia molecules. The last three all react with sulphuric acid.

8 Add 4 mol dm^{-3} sulphuric acid (**CARE** Corrosive), 1 cm^3 at a time, to the beaker with stirring (glass rod). During this addition there will be some effervescence and a precipitate will form. Keep on adding the acid until the precipitate just dissolves.

d **i** What gas has caused the effervescence? How could you identify this gas?
ii What colour is the precipitate? What do you think the precipitate might be?
iii Write equations for the reactions of sulphuric acid with:
– copper(II) carbonate
– copper(II) hydroxide
– ammonia solution.

9 Use small quantities of sodium hydroxide solution (**CARE** Corrosive) and dilute sulphuric acid (**CARE** Corrosive) to adjust the pH of the solution so that it is just acidic. Filter the solution into a 250 cm^3 conical flask using a conventional filter funnel.

Finding the concentration of $Cu^{2+}(aq)$ ions in solution (Optional extension)

E1 Transfer the filtrate to a 250 cm^3 volumetric flask, and make up to the mark with water. Stopper the flask and invert it several times to mix the solution.

E2 Use a pipette and pipette filler to withdraw 10.0 cm^3 of the solution and transfer it to a 100 cm^3 conical flask.

E3 Add a spatula measure of ammonium ethanoate to the conical flask to act as a buffer (to keep the pH of the solution constant). Using a glass rod, test a drop of the mixture with Universal Indicator paper: if acidic, add more ammonium ethanoate until the mixture is nearly neutral.

E4 Add approximately 1 g (a spatula measure) of potassium iodide to the conical flask. Swirl the contents. The solution will turn brown due to the formation of iodine and a beige coloured precipitate of copper(I) iodide will appear.

E5 Fill a burette with 0.100 mol dm^{-3} sodium thiosulphate solution. Make sure that the burette jet is also full of solution.

E6 Record the volume reading in the burette before starting the titration. Add the sodium thiosulphate solution, in small volumes, to the contents of the conical flask until the iodine colour is nearly dispelled. Then add 1 cm^3 of starch solution and continue the titration until the characteristic blue–black colour just goes. This is the end-point; the mixture will be a cloudy light-beige colour due to the presence of precipitated copper(I) iodide.

E7 Record the final burette reading and record the volume of sodium thiosulphate solution used. This is your rough titration.

E8 Repeat the titration two more times with further 10.0 cm^3 portions of the original solution from the volumetric flask. When you approach the end-points in these titrations, you should add the sodium thiosulphate solution dropwise until the blue–black colour goes.

E9 Transfer the remaining contents of your volumetric flask to a 250 cm^3 conical flask and continue to step **10**.

e **i** From the burette readings which agree to within 0.2 cm^3, work out the average volume of sodium thiosulphate solution used in a titration.

ii Calculate the amount (in moles) of sodium thiosulphate which just reacts with the iodine in the titration flask. This amount is equal to the amount (in moles) of $Cu^{2+}(aq)$ ions in the titration flask.

Your teacher may discuss the redox chemistry involved in this titration, which explains why the amount (in moles) of $Cu^{2+}(aq)$ ions is the same as the amount (in moles) of sodium thiosulphate used.

iii Calculate the amount (in moles) of $Cu^{2+}(aq)$ ions extracted in this experiment.

iv Calculate the mass of copper extracted from the roasted ore. What appears to be the percentage by mass of copper in the roasted ore sample? (See question **g**.)

Producing and weighing the copper

10 Add zinc dust to the solution in the flask in small quantities with swirling until it is no longer blue and all the copper has been displaced from the solution.

11 The solid you obtain will contain unreacted zinc. Remove this by adding 4 mol dm^{-3} sulphuric acid (**CARE** Corrosive), 1 cm^3 at a time with swirling, until there is no further effervescence. (You may need to leave this overnight to ensure complete reaction.)

12 Filter off the displaced copper using vacuum filtration.

13 Wash the copper twice with 10 cm^3 portions of distilled water and twice with 10 cm^3 portions of propanone (**CARE** Highly flammable). On each occasion turn off the vacuum to give the liquid time to soak into the copper.

14 Allow air to be sucked through the copper to carry away any propanone as vapour; then spread out the copper on a weighed watch-glass and leave it to dry thoroughly.

15 Record the mass of the dry copper you have produced.

f If you assume that you have extracted all the copper that was present, what appears to be the percentage by mass of copper in the ore sample you used?

Evaluation of your results and procedures (Optional extension)

g If you did the optional extension, compare your answer to **f** (remember to allow for the volume of solution you removed to do the titration!) with that of **e iv**. Which method do you think will have produced the more accurate result? Explain your answer.

h In practice you have *not* extracted all the copper in the sample. What do you consider to be the main source of loss of copper in your process?

M2.4

Finding out how much acid there is in a solution

In this activity you use the technique of titration to analyse a solution of dilute sulphuric acid, and you calculate the concentration of acid it contains. This concentration is considerably greater than the concentration of acid in 'acid rain', but the same method of analysis could be used to determine accurate values of pH for 'acid rain' samples. You may find it helpful to look back at your notes on* Activity EL2.1 *in which you first performed a titration.

The questions at the end of this activity draw your attention to some of the environmental consequences of the production of sulphur dioxide from smelting.

Requirements

- solution of 'acid rain' (dilute sulphuric acid) (50 cm^3)
- sodium hydroxide solution, 0.01 mol dm^{-3} (100 cm^3)
- 100 cm^3 conical flask
- 10 cm^3 pipette
- pipette filler
- burette
- Phenolphthalein indicator solution

Phenolphthalein indicator

HIGHLY FLAMMABLE

CARE Eye protection must be worn.

WEAR EYE PROTECTION

What you do

1 Use a pipette and pipette filler to transfer 10.0 cm^3 of the 'acid rain' sample to a 100 cm^3 conical flask. Add 5 drops of Phenolphthalein indicator.

2 Fill a burette with 0.01 mol dm^{-3} sodium hydroxide solution. Make sure that the burette jet is also full of solution.

3 Record the volume reading in the burette before starting the titration. Then add sodium hydroxide solution, in small volumes, to the 'acid rain' solution in the conical flask. Swirl the flask after each addition.

4 Phenolphthalein indicator is colourless in acidic solution but pink in alkaline solution. Run in the small volumes of sodium hydroxide solution until you first observe the appearance of a *permanent* pink colour in the titration mixture. This is the end-point.

5 Record the final burette reading and calculate the volume of sodium hydroxide solution you have used.

6 Your first attempt will be a rough titration; you will have gone beyond the end-point and added more sodium hydroxide than is needed to react with all the acid in the flask. You should, however, now have a general idea of what the end-point is. Do several more titrations until you record three volumes that agree to within 0.1 cm^3. When you get near the end-points of these titrations, you should add the sodium hydroxide carefully, adding only one drop of solution at a time until the permanent pink colour is produced. Record your results in a table like the one below.

Titration	rough	1	2	3	4	5
final burette reading						
initial burette reading						
titre						

Average titre = cm^3

Working out the acid concentration

7 From the titres which agree to within 0.1 cm^3, work out the average volume of sodium hydroxide solution used in the titration.

8 Combine this average volume with the concentration of the sodium hydroxide solution to calculate the amount (in moles) of sodium hydroxide, NaOH, which just reacts with the acid in the titration flask.

9 The acid in the 'acid rain sample' is sulphuric acid. The equation for the reaction in this titration is therefore:

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

Calculate the amount (in moles) of sulphuric acid, H_2SO_4, in the flask in each titration.

10 The titration flask contained 10.0 cm^3 of sulphuric acid solution. Calculate the amount (in moles) of acid which would be contained in 1 dm^3 (1000 cm^3) of solution. Write down the concentration of the sulphuric acid in units of mol dm^{-3}.

Evaluating your results and procedures

a What is the percentage error for each of the measurements you made? Look at your notes on **Activity EL2.1** if you need help with this.

b Which is the most important of these errors? Check that the number of significant figures you used in your answer to step **10** is consistent with the least precise of the measurements you made.

c Explain how aspects of your procedure were designed to ensure that your results were as accurate and reliable as possible.

Sulphur dioxide from smelting

d The equation for smelting chalcopyrite at Bingham Canyon is:

$$4CuFeS_2 + 10\tfrac{1}{2}O_2 \rightarrow 4Cu + 2FeO + Fe_2O_3 + 8SO_2$$

i What amount (in moles) of sulphur dioxide, SO_2, is produced for each mole of copper, Cu?

ii What is the relationship between the masses of 1 mol of SO_2 and 1 mol of Cu? (A_r: O, 16; S, 32; Cu, 64)

iii How many tonnes of sulphur dioxide are produced per tonne of copper?

e 200 000 tonnes of rock with an average copper content of 0.5% by mass are mined every day at Bingham Canyon. In the US the maximum permissible concentration of sulphur dioxide in the air in any one day is 0.365 tonnes km^{-3}.

i How many tonnes of sulphur dioxide are produced daily at the Bingham Canyon smelter?

ii What volume of air would become contaminated each day to the maximum permissible level if this sulphur dioxide were allowed to escape? Perhaps you can now see why the sulphur dioxide is converted into sulphuric acid, even though the acid is worth less than the cost of extracting the sulphur dioxide.

M2.5

The philosopher's microbe?

In the Middle Ages, alchemists dreamed of the 'philosopher's stone', a substance which would be able to convert ordinary metals, like lead, into gold. This activity tells you about a technique which almost turns ordinary rock into gold. It illustrates an application of bacterial leaching, and gives you an opportunity to practise and develop your reading and communication skills.

Read the report that follows, which is based on an article written by Dr Jack Barrett, formerly of the Department of Chemistry at King's College, London (KCL), then answer the questions below.

(Arseno-pyrites is FeAsS. The oxides of arsenic, As_2O_3 and As_2O_5, are volatile and toxic. Their emission is very strictly controlled.)

To get at the gold it is important to break down the pyrites.

Answers lie in the spoil

Salmonella and *Listeria* notwithstanding, bacteria can be good for you, especially if you own a goldmine with ore containing pyrites in a country which objects to sulphur and arsenic being poured into its atmosphere.

Researchers at King's College, London, have isolated and harnessed a unique community of microbes that has been working in Australia in the first major, commercially viable application of a technology known for a quarter of a century but yet to realise its full potential: bacterial leaching.

The biotechnology of using microbes to release residual metal from low-grade ores, whose treatment by conventional physical and chemical processes entails unacceptably high levels of pollution, has become routine in American copper mining. There *Thiobacillus ferro-oxidans* happily chews its way through spoil-heaps that were once useless. *T. ferro-oxidans* produces acid which helps the bacteria to liberate soluble copper compounds. When scrap-iron is added to the resulting solution metallic copper is produced – as satisfying a piece of internal economy as one is likely to come across in industry.

T. ferro-oxidans also uses its bizarre metabolism to turn pyrites (iron sulphides) and arseno-pyrites into iron oxides. When it has done that, any metal (such as gold) previously encapsulated in the sulphide can be recovered by the application of chemicals in the normal way.

Gold may be found mixed in with oxide or sulphide ores of other metals. The problem is – how to get the gold out? If the gold occurs with oxide ores it is normally extracted by treating them with cyanide. But this isn't much good for sulphide ores like pyrites because cyanide only gets at as little as 10% of the encapsulated gold. Bacteria can expose 85–100% of the latter to extraction by cyanide.

A process known as roasting can also turn pyrites into oxide – but only at the cost of sending noxious sulphur dioxide and arsenious oxide up the chimney in increasingly unacceptable quantities. Nearly all mining countries now restrict roasting so severely that it is no longer commercially viable.

Biotechnology is already being tried in the gold-mining industry, but so far with mostly equivocal results; subsidiary equipment and procedures may be inadequate, tending to give the new technology as a whole a bad name. The principal problem with *T. ferro-oxidans* is that it is fussy about its ambient temperature, preferring about 30 °C for optimum performance.

Unfortunately, many mining regions are naturally hotter than that, to say nothing of the heat generated by the process itself: the cost of reducing and holding the temperature to the required level can make the process forbiddingly expensive.

The KCL team believe their new bacterial culture has the edge because it will cheerfully work in temperatures between 30 and 50 °C degrees, eliminating the need for cooling. On this basis, says Dr Jack Barrett, inorganic chemist on the team, the KCL process takes considerably less capital as well as having lower running costs than other methods.

The KCL researchers know little enough about their microscopic prodigy beyond what it does. It eats pyrites as if they were going out of fashion and converts them into oxides (biooxidation) so that the previously encapsulated gold can be extracted conveniently by dissolution in cyanide, followed by recovery through precipitation.

What the microbes need is an environment roughly as acidic as battery-acid, access to oxygen and carbon dioxide from the air, and the right temperature. Their major peculiarity is that they need no organic nourishment of any kind but live exclusively on inorganic matter. Alchemists would clearly have done better to look for a philosopher's microbe.

The organisms were isolated from water samples found by KCL microbiologist Professor Robert Poole at an Australian mine in 1986. The resulting mixed culture appears to combine the best qualities of its components, most notably the broad temperature-tolerance which Dr Barrett believes to be its major selling point.

The KCL team got into the gold-recovery business by accident. Dr Barrett's wife Eileen, who works for the Mineral Industry Manpower and Careers Unit, asked him to find out whether gold could be extracted from pyrites from an old Welsh mine. He made the research a project for his third-year students, involving a series of chemical experiments. It was only at the end of the programme that his inorganic chemist colleague, Dr Martin Hughes, suggested the microbiological approach – with encouraging results.

'What happened next is only too familiar,' said Barrett. 'We could not find any cash in Britain to exploit the discovery, but fortunately we eventually got a positive response in Australia.' He believes that he and his colleagues collided not only with the customary conservatism of British venture-capital, but also a subconscious prejudice against using organisms in industrial processes.

'People must wonder what would happen if they escaped, as in some old horror film, or perhaps they think such bacteria are infectious. But they can't "escape" and they aren't interested in organic matter,' he says.

An Australian mining firm funded a pilot plant which worked successfully. A full-scale plant was built in Western Australia and opened in 1994 treating up to 5 tonnes of gold concentrate per hour. In 1998 the Australian and British governments decided to sell off major proportions of their gold reserves, causing the gold price to fall well below the $300 per ounce level and making the treatment of refractory ores uneconomic. The bacterial plant was closed and no further plants have been opened.

The company is now using the bacterial technology to treat copper and nickel concentrates in a plant in Mexico and expects expansion in the extraction of base metals while awaiting better times which would allow a return to gold extraction.

The implications of the technology once it is established are enormous. Unless geological upheavals have supervened, oxide ores are found nearest the surface, because that is where the oxygen is, and sulphide ores are underneath. The difficulties of extracting gold from the latter have commonly meant abandoning mining when the sulphide level is reached.

After munching through the arseno-pyrites the KCL culture leaves ferric arsenate behind – an insoluble, stable and environmentally neutral residue which piles up just as iron oxide does at the end of the conventional gold-extraction process.

a Suggest a reason why the gold is encapsulated in the veins of pyrites and not spread out in the rock.

b What is the major obstacle to using bacterial leaching in the metal extraction industry?

c List three chemicals needed by *T. ferro-oxidans* besides a supply of pyrites.

d Explain why the use of *T. ferro-oxidans* poses no threat to life or to other organic matter.

e Explain why using biotechnology of this kind may give 'new life to old mines'.

This activity helps you to find out about the very different properties of substances which have covalent bonds.

What you do

Construct a table like the one below, but leave about 5 cm depth for each substance. Fill in your table by consulting textbooks, databooks, CD ROMs, the Internet, Intranet, etc. List the sources that you consulted and give a detailed reference (author, year of publication, title, publisher, page number) for each diagram.

Substance	Formula	Properties			Diagram of structure
		melting point/K	boiling point/K	solubility in water	
carbon monoxide					
carbon dioxide					
hexane					
diamond					
silica (silicon(IV) oxide)					

QUESTIONS

a Carbon dioxide has a simple molecular structure – covalently bonded molecules with weak intermolecular forces between them. Diamond has a giant covalent structure – a network of covalent bonds throughout.

What type of structure has:
i carbon monoxide?
ii silica?
iii hexane?

b Explain why giant covalent (network) structures have very high melting points but molecular structures have low ones.

c If carbon dioxide is cooled below its melting point it solidifies to produce a white solid – dry ice. This can be cut with a steel knife whereas diamond and silica cannot. Give a step by step explanation of these observations suitable for a student who has not studied chemistry beyond GCSE.

M3

Check your notes on *From Minerals to Elements*

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

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

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

- Calculations involving concentrations of solutions.
- The classification of elements into s, p and d blocks.
- The electronic configuration of atoms from hydrogen to krypton in terms of main energy levels and s, p and d atomic orbitals.
- The following physical properties of the halogens: appearance and state at room temperature, volatility, and solubility in water and organic solvents.
- Assigning oxidation states to the elements in a compound and the use of oxidation states to decide which species have been oxidised and which reduced in a redox reaction.
- Redox reactions of s- and p-block elements in terms of electron transfer, using half-equations to represent the oxidation and reduction reactions.
- The redox changes which take place when chlorine, bromine and iodine react with other halide ions and the relative reactivity of the halogens.
- The redox changes occurring in the extraction of bromine from sea water (**Storyline M1**; **Activity M1.2**)
- The reaction between halide ions and silver ions.
- How a hazardous substance like bromine is handled and transported (**Storyline M1**; **Activity M1.4**).
- The economic importance of bromine and chlorine and their compounds (**Storyline M1**).
- The structure of an ionic lattice, eg sodium chloride.
- Writing ionic equations to represent precipitation reactions and other reactions involving ionic compounds.
- The hydration of ions in aqueous solution.
- The major stages in the extraction of a pure metal from its ore (**Storyline M2**).
- The environmental implications of mineral extraction (**Storyline M2**).
- Flow diagrams for chemical processes (**Storyline** in general).
- Recognising from the balanced equation for a reaction whether it is an acid–base, redox or precipitation reaction.
- Identification of the proton donor and proton acceptor in an acid–base reaction.
- The procedure for carrying out an acid–alkali titration and how to work out the results (**Activity M2.4**).
- The procedure for vacuum filtration (**Activity M2.3**).
- Examples of giant covalent (network) structures, such as diamond and silicon(IV) oxide (**Activity M2.6**).
- Interpreting differences in the physical properties of CO_2 and SiO_2 in terms of their different structures (**Activity M2.6**).

A2.1

What substances can act as sunscreens?

In this activity, you will use information about the absorption of visible and ultraviolet radiation by some substances to decide how they will affect radiation from the Sun.

Look at Figure 1, which shows the portion of the Sun's radiation that reaches us on Earth, and its effect on skin.

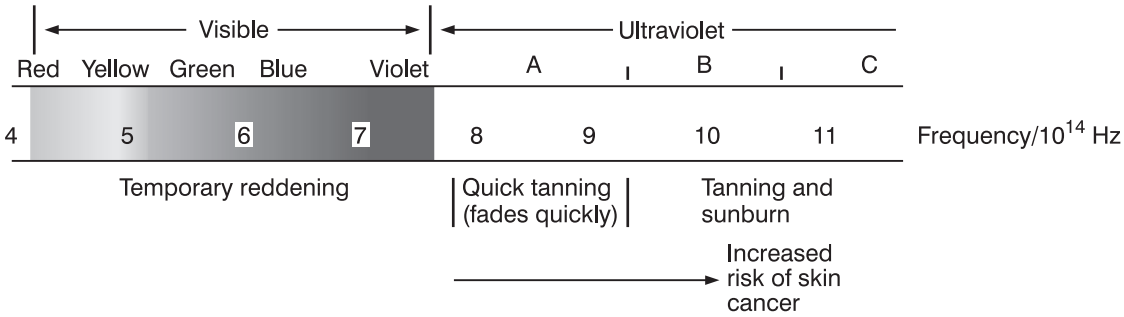


Figure 1 The portion of the Sun's radiation that reaches the Earth and its effect on the skin (from **The Atmosphere**, **Storyline A2***)*

Each of the substances listed in Table 1 absorbs light in the visible–ultraviolet region. The **absorption spectrum** of each substance shows the intensity of radiation absorbed at each frequency, and may consist of either a number of sharp peaks or a broad band of absorption called a continuum. The figures in Table 1 show the lowest frequency (or frequency range) at which each substance absorbs strongly.

Substance	Absorption frequency range/10^{14} Hz
water	from 16.2
glass	from 9.4
glyceryl trioleate (a major constituent of olive oil)	6.8–10.7
4-aminobenzoic acid	8.8–12.2

Table 1 Ultraviolet absorption of some substances

Where possible, mark on Figure 1 the start of the absorption range of the substances in the table above. (Some of them may lie outside the frequency range shown in the diagram.)

What are your conclusions concerning:

a whether swimming can protect you from sunburn?
b the chance of getting tanned sitting in a south-facing window on a sunny day?
c the use of olive oil as a sunscreen?
d the use of 4-aminobenzoic acid as a sunscreen?

A2.2 Investigating sunscreens

This activity will help you develop the important skill of designing and carrying out a practical investigation.

Requirements

- a light source which provides radiation of about the same frequency as the ultraviolet light that causes sunburn and skin cancer
- a means of supporting the sunscreen so that light can be directed at it and possibly pass through it
- a way of detecting the ultraviolet light
- a variety of sunscreen products with different screening factors

CARE If you are using any kind of ultraviolet lamp, remember that **ultraviolet radiation is hazardous**. Follow the recommended precautions concerning eye protection.

What you do

The aim of this activity is to find out about the effectiveness of different sunscreens.

The design of the experiment is left to you. You will need to think about the items in the requirement list, and decide how you are going to test the sunscreens so that you can make fair comparisons. You may decide on modifications after your first try which lead to improvements in your method.

Prepare a **Risk Assessment** for your planned activity and a list of sources you have used in developing your plan and your Risk Assessment.

Do not start your investigation until your plan has been checked by your teacher.

The following points may help you.

1 The best source of ultraviolet radiation of the right frequencies is of course the Sun itself. A domestic sun-tan lamp is also good, but does not emit frequencies above about 9.3×10^{14} Hz. A mid-range ultraviolet lamp from the school science department will emit frequencies in the 9.3×10^{14} Hz – 10.7×10^{14} Hz region, where the skin is very sensitive.

2 Most ultraviolet radiation will not pass through glass. It passes quite well through perspex, and very well through clingfilm.

3 For detecting the ultraviolet radiation, there are a number of possibilities:

- **a** Ultraviolet sensitive paper, which turns blue in the presence of natural ultraviolet radiation. (Incidentally, this paper is used to make security passes to check whether the wearer has left the building. You can use it to test the effectiveness of glass as a sunscreen by sticking pieces inside and outside a window.)
- **b** A white cloth that has been washed in detergent. (Most machine detergents contain fluorescent compounds. You can see the effect under some disco lights.) The cloth will give a bright fluorescence with ultraviolet light.
- **c** Tonic water fluoresces in ultraviolet light.
- **d** Some photocopying paper fluoresces.

A2.3

What is the effect of the atmosphere on the Sun's radiation?

In this activity, you will use information about the ultraviolet absorption of some atmospheric gases to investigate their effect on radiation from the Sun.

Figure 1 shows the spectrum of the Sun's radiation in space, that is before it has passed through the Earth's atmosphere. It shows the energy emitted at each wavelength (and frequency).

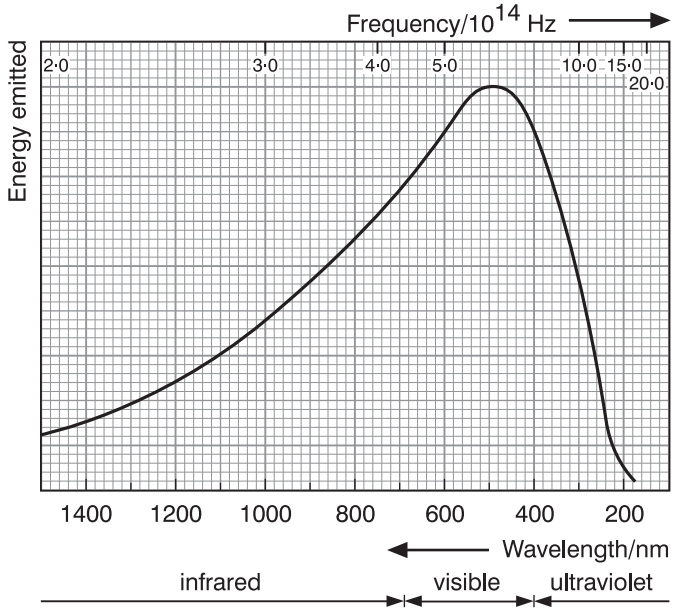


Figure 1 The spectrum of solar radiation in space

Table 1 shows the frequency and wavelength ranges over which some common atmospheric gases absorb ultraviolet radiation. Where only one figure is given, it represents the low frequency (high wavelength) limit at which absorption begins.

You will find it easier to use the wavelength ranges rather than the frequency ranges. This is because the horizontal axis of the spectrum is plotted using a linear wavelength scale, whereas the frequency is non-linear.

Gas	Absorption frequency range/10^{14} Hz	Absorption wavelength range/nm
oxygen	12.4–17.1 (very weak) and above 17.1 (strong)	242–175 (very weak) and below 175 (strong)
nitrogen	above 50.0	below 60
water	16.2–20.6	185–145
carbon dioxide	17.6–23.9 (weak) and above 25.6	170–125 (weak) and below 117
ozone	10.1–14.0	296–214
methane	above 20.8	below 144
sulphur dioxide	9.1–12.5 (weak) and above 13.8	330–240 (weak) and below 217

Table 1 Ultraviolet absorption of some atmospheric gases

1 On Figure 1 shade the area of the solar spectrum which corresponds to ultraviolet radiation.

2 List the gases from Table 1 that absorb in this region, with the relevant absorption ranges. Mark and label these regions on Figure 1 using a double-headed arrow ↔.

a Comment on the effect of each of the gases in the atmosphere on solar radiation. You should consider both the absorption characteristics and the concentrations of the gases in the atmosphere.

b How would you expect the Sun's spectrum as seen on the surface of the Earth to differ from that seen in space?

A3.I

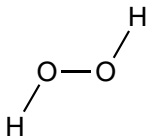
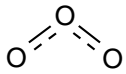
More about ozone

In this activity, you can find out more about the bonding in ozone and the stability of ozone relative to oxygen. You can remind yourself about the use of bond enthalpies to calculate enthalpy changes.

Ozone is a polymorph (or allotrope) of oxygen. Its formula is O_3 and it is called trioxygen. It is a pungent-smelling, pale blue gas which condenses at low temperatures to give a dark blue liquid. It is much less abundant in the atmosphere than the other polymorph, dioxygen, O_2.

Bonding in ozone

The table shows three substances which contain oxygen–oxygen bonds.

Substance	Shape of molecule	Length of O–O bond/nm	Bond enthalpy of O–O bond /kJ mol^{-1}
dioxygen, O_2 (double bond)			
hydrogen peroxide, H_2O_2 (single bond)			
ozone, O_3			

a Use the **Data Sheets** to fill in the bond length and bond enthalpy of the oxygen–oxygen bond in each compound.

b What do these figures tell you about the nature of the bonding in ozone?

Energetics

The overall equation for the formation of ozone from dioxygen is:

$$1\tfrac{1}{2}O_2(g) \rightarrow O_3(g)$$

c Work out the standard enthalpy change of formation of ozone by the following steps.

i Draw a Hess cycle to show the formation of ozone from dioxygen via three atoms of oxygen in the gaseous state.

ii Use the bond enthalpies in your table to work out a value for the standard enthalpy change of formation of ozone. (Remember that the bond enthalpy is the energy needed to break one mole of bonds, see **Chemical Ideas 4.2**.)

d Which is the more energetically stable allotrope of oxygen, O_2 or O_3? Explain your answer.

e Ozone is described as an *endothermic substance*. What does this mean?

f Would you expect ozone to be more or less reactive than dioxygen? Explain your answer.

A3.2

The photodissociation of bromine (Optional teacher demonstration)

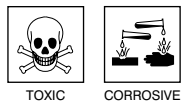
In this activity you will investigate the effect of light on the reaction between bromine and hexane. You will learn how to handle bromine safely.

Requirements

- hexane (6 cm^3)
- bromine (3 drops)
- aluminium foil
- test-tubes and rack
- Universal Indicator paper
- glass rod
- concentrated ammonia solution
- light source (sunlight is best, but you could use a strong lamp such as a fluorescent light tube – a microscope lamp or an overhead projector lamp will work reasonably well)

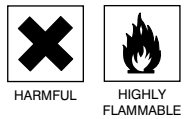
CARE Bromine liquid should always be used in a fume cupboard. It produces an irritant vapour which is very toxic. The liquid causes severe burns. A beaker of sodium thiosulphate solution (approximately 1 mol dm^{-3}) should be available to treat spillages.

bromine



concentrated ammonia solution

hexane



CARE Eye protection and gloves must be worn.

What you do

1 Put 2 cm^3 of hexane in each of three test-tubes. (**CARE** Hexane is highly flammable and harmful. Avoid skin contact and do not breathe the vapour.)

2 Add one drop of bromine (not bromine water) to each tube. (**CARE** Bromine is corrosive and toxic. Wear eye protection and gloves. Work in a fume cupboard when adding the bromine.)

3 Wrap aluminium foil around two of the tubes as shown in Figure 1. Stand the three tubes side by side in a test-tube rack.

4 Leave the rack in bright sunlight or next to a bright light source for 5–10 minutes, then examine the appearance of each tube. Cautiously blow across the top of each tube. Test any gases given off with moist indicator paper, and by holding a drop of ammonia solution on a glass rod at the mouth of the test-tube.

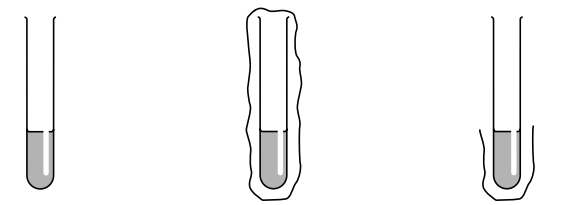


Figure 1

QUESTIONS

a What evidence is there that bromine undergoes photodissociation?

b Look up the values for Br–Br and C–H bond enthalpies. Remember that bond enthalpies are given per mole of bonds. Calculate the enthalpy change when:

i one Br–Br bond is broken
ii one C–H bond is broken.

Use $E = h\nu$ to calculate the frequencies of photons of radiation corresponding to each of these energies. Which bond is most likely to be broken by absorption of sunlight?

c What has the bromine reacted with?

d What is the gaseous product that is formed?

e Write an equation, with state symbols, for the reaction of this gas with ammonia.

A3.3

Investigating the reaction between bromine and cyclohexane

In this activity you will carry out a quantitative investigation of the reaction between bromine radicals and cyclohexane, and determine the amount of one of the products formed. This will give you an opportunity to improve your skills at carrying out an accurate titration, and to use the results of a titration to calculate the information needed.

Requirements

- reagent bottle (about 250 cm^3 capacity) with good-fitting stopper
- cyclohexane (35 cm^3)
- protective gloves
- distilled water
- bromine (1 g)
- marked pipette for adding bromine
- sodium hydroxide solution, 0.200 mol dm^{-3} (100 cm^3)
- Phenolphthalein indicator solution
- burette and stand
- wash bottle with distilled water
- access to a balance
- light source (sunlight is best, but you could use a strong lamp such as a fluorescent light tube – a microscope lamp or an overhead projector lamp will work reasonably well)

CARE Bromine liquid should always be used in a fume cupboard. It produces an irritant vapour which is very toxic. The liquid causes severe burns. A beaker of sodium thiosulphate solution (approximately 1 mol dm^{-3}) should be available to treat spillages.

bromine


TOXIC


CORROSIVE

cyclohexane


HIGHLY FLAMMABLE

dilute sodium hydroxide solution


IRRITANT

Phenolphthalein indicator solution


HIGHLY FLAMMABLE

CARE Eye protection and gloves must be worn.


WEAR EYE PROTECTION


WEAR PROTECTIVE GLOVES

Outline of the experiment

Bromine is added to a mixture of cyclohexane and water, and the mixture is placed in a bright light and shaken from time to time. Hydrogen bromide (HBr) is formed, and passes into the water layer.

When all the bromine has reacted and the red colour has gone, the mixture is titrated with sodium hydroxide. HBr(aq) reacts with the sodium hydroxide, and from the titration result the amount of HBr formed per mole of bromine can be calculated.

What you do

1 Put 35 cm^3 of cyclohexane and 15 cm^3 of distilled water in the bottle and stopper it firmly. (**CARE** Cyclohexane is highly flammable. Avoid skin contact and do not breathe the vapour.)

2 Make sure the bottle is dry on the outside, then find the mass of the bottle, stopper and contents.

3 Add approximately 1 g (about 0.3 cm^3) of bromine to the bottle. (**CARE** Bromine is corrosive and toxic. Wear eye protection and gloves. Work in a fume cupboard when adding the bromine. Do not remove the stopper from the bottle after the bromine has been added.)

4 Find the mass of the bottle again, in order to find the exact mass of bromine added.

5 Shake the bottle. Place it near a light source or on a window sill. Shake the bottle every 2 minutes until the colour has disappeared.

6 Fill a clean burette with 0.200 mol dm^{-3} sodium hydroxide solution. (**CARE** Sodium hydroxide of this concentration is an irritant.)

7 Give the stoppered bottle a final shake, remove the stopper and rinse it with distilled water into the bottle so no liquid is lost.

8 Add 10 drops of Phenolphthalein to the bottle. Titrate the contents of the bottle with 0.200 mol dm^{-3} sodium hydroxide solution to a faint pink end-point. The end-point is not very stable and the colour tends to fade. Titrate to the first *overall* pink colour. (**CARE** The product of the reaction is flammable. Its vapours are harmful and may irritate the eyes and nose. Avoid breathing the vapours.)

9 When you have finished, the reaction mixture must be poured into a residue bottle *in a fume cupboard*.

Using the results

Record your results in a suitable table, then answer the following questions.

a What mass of bromine did you use?

b What amount in moles of bromine, Br_2, did you use?

c What volume of sodium hydroxide solution was needed in the titration?

d What amount in moles of sodium hydroxide, NaOH, was used in the titration?

e Write an equation for the reaction between sodium hydroxide and hydrogen bromide.

f What amount in moles of hydrogen bromide was produced in the reaction between bromine and hexane?

g What amount in moles of hydrogen bromide would be produced from the reaction of *1 mole* of bromine, Br_2?

h Write a balanced equation for the reaction between hexane and bromine to produce bromohexane, $C_6H_{11}Br$.

i What general type of reaction is this?

j Why was water added to the reaction mixture, even though it is not a reactant?

k Bromohexane is formed in this reaction. In which of the two layers would it be found?

Evaluating your results and procedures

l For which of your measurements is the level of precision you could achieve important? Work out the percentage error for each of these measurements.

m Compare the relative importance of each of these errors.

n Identify the stages in your *procedure* which could have led to errors.

o How do you think the sources of error or uncertainty that you have identified in **l** and **n** affect the accuracy and reliability of your overall result?

A4.1a

How do halogenoalkanes differ in reactivity?

This part of the activity will allow you to practise and develop your skills in experimental design. You are asked to plan an experiment to compare the reactivity of some halogenoalkanes.

Some background information

Halogenoalkanes have the general formula RHal, where R is an alkyl group and Hal is a halogen atom. In this experiment you will investigate how the reactivity of halogenoalkanes depends on the nature of the halogen atom, Hal.

You will compare the rates of hydrolysis (reaction with water) of 1-chlorobutane, 1-bromobutane and 1-iodobutane.

$$CH_3CH_2CH_2CH_2Hal + H_2O \rightarrow CH_3CH_2CH_2CH_2OH + H^+ + Hal^-$$

The rate of the reaction is followed by carrying it out in the presence of silver ions, $Ag^+(aq)$. Silver ions react with halide ions to form a precipitate of silver halide:

$$Ag^+(aq) + Hal^-(aq) \rightarrow AgHal(s)$$

Halogenoalkanes are covalently bonded, so they give no precipitate with silver ions. But as the reaction proceeds and halide ions are produced, a white or yellow precipitate of silver halide gradually appears.

Halogenoalkanes are insoluble in water, so the reaction is carried out in the presence of ethanol, which acts as a mutual solvent for the halogenoalkane, the water and the silver ions.

Planning

Write a plan for how you will compare the rate of hydrolysis of a few drops of the three halogenoalkanes by warm water. Your plan should include the following:

- the apparatus to be used
- the quantities of materials to be used
- details of what you expect to do in the form of a set of instructions that could be followed by another student without any further guidance
- a **Risk Assessment** which identifies the hazards associated with each substance you will use and each operation you will carry out, and what steps you will take to minimise the hazards
- details of the sources you have used in devising your plan and your Risk Assessment.

Do not carry out your plan until it has been checked by your teacher.

A4.1b

How do halogenoalkanes differ in reactivity?

In this part of the activity, you will carry out the experiment to compare the reactivity of some halogenoalkanes. From your results, you should be able to see why Midgley was led to look at CFCs for a refrigerant gas.

Requirements

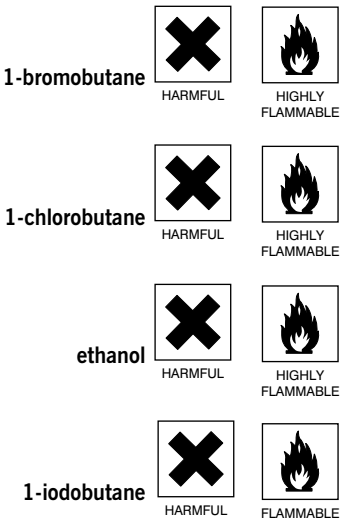
- test-tubes
- ethanol (3 cm^3)
- silver nitrate solution, 0.01 mol dm^{-3} (3 cm^3)
- 0–110 °C thermometer
- 250 cm^3 beaker
- source of hot water (50 °C)
- 1-chlorobutane
- 1-bromobutane
- 1-iodobutane

} a few drops of each

- stopclock

CARE Eye protection must be worn.

WEAR EYE PROTECTION



Some background information

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You will compare the rates of hydrolysis (reaction with water) of 1-chlorobutane, 1-bromobutane and 1-iodobutane.

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Halogenoalkanes are covalently bonded, so they give no precipitate with silver ions. But as the reaction proceeds and halide ions are produced, a white or yellow precipitate of silver halide gradually appears.

Halogenoalkanes are insoluble in water, so the reaction is carried out in the presence of ethanol, which acts as a mutual solvent for the halogenoalkane, the water and the silver ions.

What you do

1 Heat some water to about 50 °C in a beaker. Extinguish the flame. (Alternatively, the water can be heated safely using an electric kettle.)

2 Set up three test-tubes labelled **1**, **2**, **3**. Place 1 cm^3 of ethanol into each. (**CARE** Ethanol is highly flammable. Keep bottles stoppered when not in use and well away from naked flames. Avoid skin contact and do not breathe the vapour.)

3 Add 2 drops of chlorobutane to tube **1**, 2 drops of bromobutane to tube **2**, and 2 drops of iodobutane to tube **3**. (**CARE** Halogenoalkanes are flammable. Their vapours are irritating and harmful. Avoid inhaling them.)

4 Stand the tubes in the beaker of water at 50 °C. Put three test-tubes, each containing 1 cm^3 of 0.01 mol dm^{-3} silver nitrate solution, in the same beaker. Leave the tubes for about 10 minutes so that they reach the temperature of the bath.

5 Now add 1 cm^3 of the warm silver nitrate solution to each of tubes **1**, **2** and **3**, working quickly and noting the time. Shake each tube to mix the contents.

6 Observe the tubes over the course of the next 5 minutes or so and note down the time when any precipitate appears.

RESULTS AND QUESTIONS

If a precipitate appears it means that hydrolysis has taken place and halide ions have been released from the halogenoalkane.

a Which halogenoalkane undergoes the fastest hydrolysis? Which is slowest?

b Suggest a reason for the different rates of hydrolysis. The chart showing bond enthalpies in the **Data Sheets** may help you.

c What result would you predict for 1-fluorobutane? Explain your answer.

d Why was the experiment done using halogenobutanes rather than halogenomethanes?

e What bearing do your results have on the choice of the best halogenoalkanes to use as refrigerant fluids?

A4.2

Making a halogenoalkane

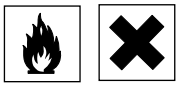
In this activity, you will prepare a sample of 2-chloro-2-methylpropane. This will involve learning new techniques both to carry out the reaction, and to separate and purify the liquid product. You will need to work carefully to obtain the maximum yield possible.

Requirements

- 10 cm^3 measuring cylinder
- 50 cm^3 measuring cylinder
- 2-methylpropan-2-ol (6.5 cm^3)
- concentrated hydrochloric acid (20 cm^3)
- access to a balance
- 50 cm^3 pear-shaped flask
- 50 cm^3 separating funnel and stopper
- distillation head
- clamps and stand
- anti-bumping granules
- condenser
- small Bunsen burner or electric heating mantle
- sodium hydrogencarbonate solution, 5% (10 cm^3)
- anhydrous sodium sulphate
- 100 cm^3 conical flask (2)
- 0–110 °C thermometer and holder
- specimen tube
- 50 cm^3 beaker

concentrated hydrochloric acid

2-methylpropan-2-ol



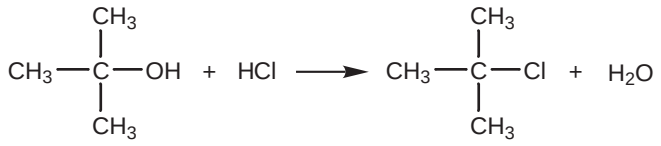
CARE Eye protection must be worn.

CARE The vapours produced in this activity can be harmful. Work in a well-ventilated laboratory and avoid inhaling the fumes.

Background

One way to make a halogenoalkane is to start with an alcohol and replace the –OH group by a halogen atom.

For example, you can make 2-chloro-2-methylpropane by allowing 2-methylpropan-2-ol to react with concentrated hydrochloric acid at room temperature. The overall reaction can be represented by the equation:



2-methylpropan-2-ol *2-chloro-2-methylpropane*

The mechanism of this reaction is explained in **Chemical Ideas 14.2**. (A similar type of reaction with HBr rather than HCl is described in **Chemical Ideas 13.1**.)

The preparation of an organic compound usually takes place in four stages:

- carrying out the reaction
- separating the required product from the reaction mixture
- purifying the product
- testing the product to check that it is a pure sample of the required compound.

a Write the equation for the reaction given above using skeletal rather than structural formulae.

What you do

Carrying out the reaction

Before you carry out the reaction you need to learn how to use the separating funnel correctly. Your teacher will show you.

1 Into a 10 cm^3 measuring cylinder, pour about 6.5 cm^3 of 2-methylpropan-2-ol. (**CARE** Highly flammable and harmful. Keep bottle stoppered when not in use and well away from naked flames. Avoid skin contact and do not breathe the vapour.) This will be approximately 5 g of the 2-methylpropan-2-ol. Weigh the measuring cylinder and contents and then pour the 2-methylpropan-2-ol into a 50 cm^3 separating funnel. Weigh the empty measuring cylinder and record the exact mass of 2-methylpropan-2-ol you have added to the funnel.

2 Into a 50 cm^3 measuring cylinder, pour about 20 cm^3 of concentrated hydrochloric acid. (**CARE** Extremely corrosive. Avoid skin contact.) Gradually add the acid to the 2-methylpropan-2-ol in the funnel over a period of about 2 minutes.

3 Put the stopper in the funnel and shake the mixture from time to time over the next 20 minutes. After each shaking *remove the stopper briefly to release the pressure*.

Separating the product from the reaction mixture

The mixture now contains the product 2-chloro-2-methylpropane (**CARE** Highly flammable and harmful) and the following substances:

- 2-methylpropan-2-ol
- hydrogen chloride (hydrochloric acid)
- water.

4 Allow the mixture to stand until two layers have separated (Figure 1). Remove the stopper and run the lower layer into a clean 100 cm^3 conical flask. Use the table of densities (Table 1) to decide which layer contains the 2-chloro-2-methylpropane.

Liquid	Density/g cm^{-3}
2-chloro-2-methylpropane	0.84
2-methylpropan-2-ol	0.78
water	1.0
concentrated hydrochloric acid	1.2

Table 1 Densities of some of the liquids present

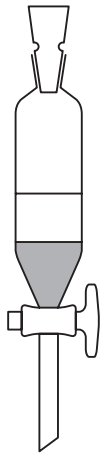


Figure 1 Separating funnel

Most of the 2-methylpropan-2-ol impurity dissolves in the concentrated hydrochloric acid layer and so is removed when you run off this layer. The remaining impurities are removed in the operations which follow.

b Suggest why the alcohol dissolves in concentrated hydrochloric acid.

c What impurities are likely still to contaminate the 2-chloro-2-methylpropane layer at this stage?

5 *Slowly* add 10 cm^3 of 5% sodium hydrogencarbonate solution to the 2-chloro-2-methylpropane in the separating funnel. Stopper the funnel and shake the contents gently and then more vigorously. *There will be a marked build up of gas, so be very careful when you release the pressure*. When the two layers have separated, run off and discard the lower aqueous layer. Repeat the washing with sodium hydrogencarbonate solution until no more gas is given off.

6 Add 10 cm^3 of distilled water and shake. When the two layers have separated, run off and discard the lower aqueous layer and then run the 2-chloro-2-methylpropane into a clean conical flask.

7 To the liquid in the flask, add a small amount of anhydrous sodium sulphate, which acts as a **drying agent** and removes the last traces of water. Add the drying agent in small quantities, swirling after each addition, until the liquid is totally clear.

d Which impurity is removed by shaking the product with a solution of sodium hydrogencarbonate?
e Why is there a marked build up of pressure during the shaking?
f Suggest a reason why sodium hydrogencarbonate solution is used rather than sodium hydroxide solution.
g How did the appearance of your product change when it was swirled with anhydrous sodium sulphate? How do you account for this?
h Name another drying agent which could be used in place of the anhydrous sodium sulphate.

Purifying the product and testing its identity and purity

Most of the impurities should now have been removed, except for a small amount of 2-methylpropan-2-ol which will be dissolved in the 2-chloro-2-methylpropane. This can be separated by carrying out a **distillation**.

8 Set up clean and dry apparatus for a simple distillation, complete with thermometer (see Figure 2). The thermometer bulb should be opposite the side-arm so that it measures the temperature of the liquid that distils over.

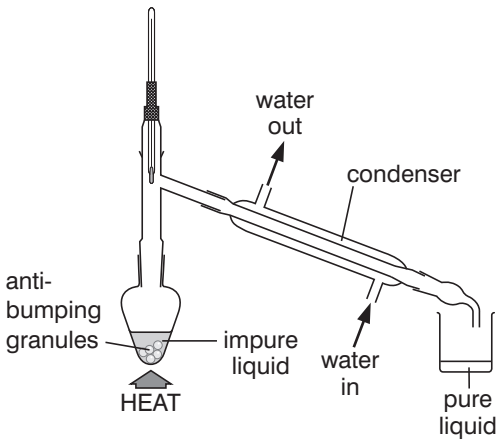


Figure 2 Apparatus for a simple distillation

9 Transfer the dried 2-chloro-2-methylpropane into the distillation flask and add a few anti-bumping granules.
10 Weigh a clean, dry specimen tube. *Gently* heat the liquid in the distillation flask using the flame from a small hand-held Bunsen burner. At first use a small beaker as the receiver. Start collecting the 2-chloro-2-methylpropane in the weighed specimen tube when the temperature reaches 48 °C. The boiling point of 2-chloro-2-methylpropane is 51 °C. Stop the distillation when the thermometer rises above 53 °C. Stopper the specimen tube and record the mass of 2-chloro-2-methylpropane collected.

i How does the final stage allow you to check the identity and purity of your product?
j Differences in three properties – solubility, acidity and volatility – are used to remove impurities from the 2-chloro-2-methylpropane. Group the impurities removed under these headings.
k Work out the **% yield** of 2-chloro-2-methylpropane as follows:
  i Write the balanced equation for the reaction used to produce 2-chloro-2-methylpropane .
  ii What is the maximum mass of 2-chloro-2-methylpropane that you could obtain from the mass of 2-methylpropan-2-ol used?
  iii Calculate the % yield you obtained in your experiment.
l Experience suggests that you will do well to get a yield over 50%. What reasons can you think of to account for a yield well under 100%?
m Look carefully at the equation for the preparation of 2-chloro-2-methylpropane. What type of reaction is this?
n What problems would you expect at each stage of the process if you were trying to scale it up to make several *tonnes* of 2-chloro-2-methylpropane?

A4.3
Designing refrigerants

In this activity you will analyse data about a number of compounds which have been considered as possible refrigerants. You will then investigate various replacements for CFCs and look at the international agreements that govern the phasing out of ozone-depleting compounds.

In the final part you are asked to produce a briefing document for a politician, which will allow you to practise your research and communication skills.

Part 1: Properties of refrigerants

Figure 1 shows an outline of how a refrigerator works.

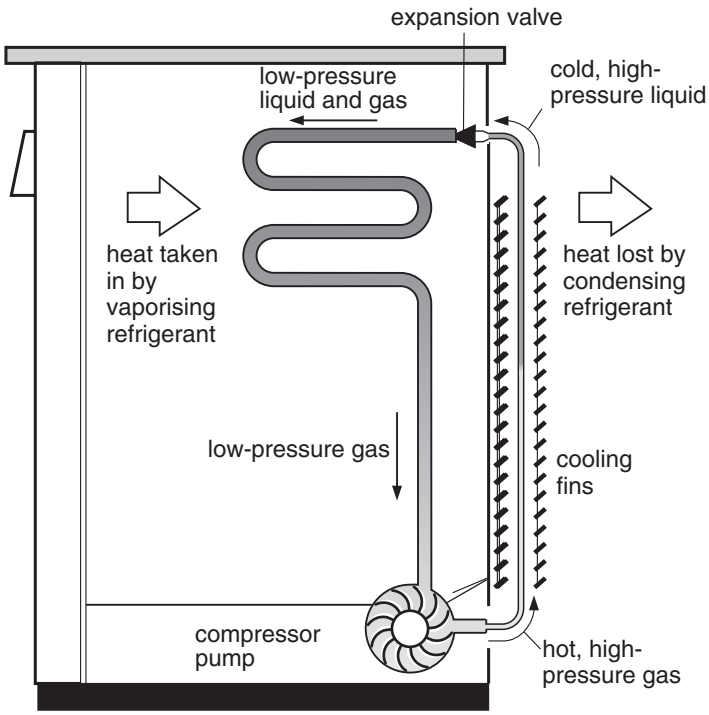


Figure 1 How a refrigerator works

The refrigerant fluid is crucial to the whole process. It must have the right boiling point – high enough to liquefy by compression, low enough to vaporise easily at reduced pressure; 240 K (–33 °C) is about right. For many years, ammonia was used as a refrigerant.

a What other properties do you think a refrigerant fluid should have?

Compounds derived from alkanes by replacing H atoms with Cl and F atoms appeared to be good candidates for refrigerant fluids. The different halogen atoms give the compounds different properties.

Table 1 gives some properties of alkanes, chloroalkanes and fluoroalkanes. Suggest answers to the following questions concerning the properties of the compounds in the table.

Formula	Boiling point/K	Chemical reactivity in atmosphere	Flammable?	Toxic?	Price
CH_4	109	moderate	yes	no	low
CCl_4	350	low	no	yes	medium
CF_4	144	very low	no	no	high
C_2H_6	185	moderate	yes	no	low
C_2Cl_6	459	low	no	yes	medium
C_2F_6	194	very low	no	no	very high
C_3H_8	231	moderate	yes	no	low
C_3Cl_8	559	low	no	yes	high
C_3F_8	237	very low	no	no	very high

Table 1 Properties of some alkanes, chloroalkanes and fluoroalkanes

b Imagine you are in the position of Thomas Midgley in 1930 and are looking for a suitable replacement for ammonia as a refrigerant fluid. You are investigating the properties of hydrocarbons and halogenoalkanes.

What are the advantages and disadvantages of each of the following in molecules of a refrigerant fluid:

i H atoms?
ii Cl atoms?
iii F atoms?

Why do you think Midgley selected CCl_2F_2 as a suitable replacement for ammonia?

Part 2: Replacing CFCs

It may help to work in small groups for this part of the activity and then compare your findings with other groups in your class.

In the late 1980s, it was shown convincingly by scientists that CFCs being used for a wide variety of purposes were damaging the ozone layer in the stratosphere. It was vital therefore that replacements were found. Just prior to the acceptance of this evidence, the annual world production of CFCs was about 8.5×10^5 tonnes.

The tables below give information about compounds containing C, H, Cl and F atoms. The three CFCs that were most widely used are shown in Table 2. Table 3 gives information about possible replacement compounds. A key to the symbols and terms used in the tables is given below the tables.

Table 2 CFCs that were widely used

Formula	Code	Uses	Toxicity	Boiling point/K	Flammable?	Ozone depletion potential	Price
CCl_3F	CFC 11	PRB*	low	297	no	1.0	medium
CCl_2F_2	CFC 12	PRB*	low	243	no	1.0	medium
CCl_2FCClF_2	CFC 113	C*	low	321	no	0.8	high

* see key below

Table 3 Possible replacement compounds

Formula	Code	Toxicity	Boiling point/K	Flammable?	Ozone depletion potential	Price
CH_2Cl_2		high	313	no	<<0.01	low
$CH_3CH_2CH_3$		low	231	yes	0	low
$CH_3CH_2CH_2CH_3$		low	273	yes	0	low
CH_3OCH_3		low	249	yes (very)	0	low
$CHClF_2$	HCFC 22	low	232	no	0.06	high
CF_3CH_2F	HFC 134a	low	247	no	0	very high
CF_3CCl_2H	HCFC 123	low	302	no	0.02	high
CH_3CCl_2F	HCFC 141b	low	305	yes	0.11	high
CH_3CHF_2	HFC 152a	?low	249	yes	0	high

Key to symbols used in the tables:

- The code is the number used in industry to identify the compound.
  HCFC: hydrochlorofluorocarbons
  HFC: hydrofluorocarbons.
- R = refrigeration and air conditioning; B = foam blowing agent; P = aerosol propellant (a minor use); C = cleaning solvent.
- The ozone depletion potential (ODP) is a measure of the effectiveness of the compound in destroying stratospheric ozone. CCl_3F is defined as having an ODP of 1.0.

QUESTIONS

c Hydrogen in the molecule results in it being degraded in the troposphere. Fluorine results in stability or inertness.

Look at the ozone depletion potentials (ODPs) of the various compounds.

i What features of a compound seem to give rise to a high ODP? Suggest a reason why.
ii What features give rise to a low ODP? Suggest a reason why.

Compare your answers and ideas with those of the other groups.

d On the basis of the information in the tables, which compound do you consider to be the most suitable replacement for:

i CCl_3F (CFC 11), for use as a blowing agent?
ii CCl_2F_2 (CFC 12), for use as a refrigerant?
iii CCl_2FCClF_2 (CFC 113), for use as a cleaning solvent?

In each case, make a shortlist of two or three, then make your final selection. Give reasons for your choices.

What further information would you need before making a final decision about replacement compounds?

Part 3: International agreements

The first major international agreement which limited production of CFCs and other ozone-depleting compounds was the *Montreal Protocol*. It was signed by thirty countries in 1987 and came into force on 1 January 1989.

The Montreal Protocol

Production of CFCs 11, 12, 113, 114, 115:

- frozen at 1986 level from 1992
- reduced to 80% from 1993
- reduced to 50% from 1998.

Production of halons (brominated halogenoalkanes used in fire extinguishers):

- restricted to 1986 levels

In 1989 the European Council of Ministers announced that CFC production would be phased out completely by the year 2000. The US made a similar declaration. Later in the year the Montreal Protocol countries (then increased to more than 60) adopted the same policy.

The Revised Montreal Protocol, London Amendment, 1990

Production of CFCs:

- reduced to 50% from 1995
- reduced to 15% from 1997
- zero by 2000.

Tetrachloromethane (used as a solvent):

- reduced to 15% from 1995
- zero by 2000.

Production of halons:

- phased out by 2000 (with some exceptions as there are no known alternatives).

1,1,1-trichloroethane (used as a solvent):

- reduced to 70% from 1995
- reduced to 30% from 1997
- zero by 2005.

HCFCs, with ODPs of about 0.05, should be used to replace CFCs in about 15% of applications, but this is seen as a transitional measure with an HCFC phase-out expected for about 2030.

1 The Montreal protocol is still under review and continues to be amended. Use Table 4 and the Internet to find out about the latest agreements for CFCs, halogenoalkanes and HCFCs. To start the search, use the Salters Advanced Chemistry web site.

2 Prepare a briefing document for a politician which:
- explains the relative merits, as refrigerants, of CFCs, HCFCs, alkanes and HFCs in terms of their constituent elements
- provides an update of international agreements on the use of CFCs and HCFCs
- identifies any outstanding problems you are aware of concerning the impact of international agreements.

Table 4 Reductions in consumption of some halogen-containing compounds required by the regulations

	Provisions of the Montreal Protocol agreed and in force at the end of 1997				**European Union regulations enacted and in force**			
	CFCs	**'Other' CFCs**	**Halons**	**HCFCs**	**CFCs**	**'Other' CFCs**	**Halons**	**HCFCs**
Base Year / **Year**	**1986**	**1989**	**1986**	**1989**	**1986**	**1986**	**1986**	**1989**
1993		20%			50%	50%	freeze	
1994	75%	75%	100%		85%	85%	100%	
1995					100%	100%		
1996	100%	100%		freeze				
2004				35%				35%
2007								60%
2010				65%				80%
2013								95%
2015				90%				100%
2020				99.5%				
2030				100%				

(Based on data given, by kind permission, in R. Powell, *Methods of Organic Chemistry* Vol. E10a, Organo-fluorine compounds, eds. B. Baasner, H. Hagermann, J.C. Tetlow. G. Thienne Verlag, 1999.)

A5

Chemistry in the stratosphere

This activity will help you record some of the information that has been presented in sections A1–A5 of this unit.

Now is the time to make sure you have a record of the main points covered in sections **A1–A5**. It is important to make these notes *as you go along*.

The following activities should help you check that you have understood the important ideas.

a Make sure you know the approximate composition of the atmosphere and the main pollutant gases.

b You have come across a lot of new terms in this part of the course, eg *stratosphere*, *radical*, *photodissociation*, *termination*. Go through the text and pick out these and others like them, then write a few lines of explanation for each, including an example taken from the text. (Don't forget to look in the **Activities** as well as in the **Storyline** and the **Chemical Ideas**.)

c Make a summary of the key points in the story concerning the function of ozone in the stratosphere, and why there is concern about the effect CFCs have on this ozone. Your summary should be no more than half a page long.

d Summarise the chemical reactions taking place in the stratosphere. You may find it helps to do this in the form of a diagram.

A6

Which are the greenhouse gases?

In this activity, you will use information about the infrared absorption of atmospheric gases to decide which will contribute to the greenhouse effect.

The frequency and wavelength ranges over which certain important atmospheric gases absorb infrared radiation are shown in Table 1.

Gas	Absorption frequency range /10^{14} Hz	Absorption wavelength range /nm
N_2	none	none
O_2	none	none
H_2O	0.43–0.64	6950–4670
CO_2	0.18–0.24	17 000–12 500
CH_4	0.39–0.46 and 0.85–1.03	7700–6500 and 3520–2900
N_2O	0.38–0.42	7800–7120
CCl_3F	0.25–0.33	12 000–9060
O_3	0.28–0.32	10 700–9340

Notes: N_2O, dinitrogen oxide, is released by many organisms. Increased use of fertilisers increases the release of N_2O.

Table 1 Infrared absorption of some atmospheric gases

The spectrum in Figure 1 shows the infrared radiation emitted by the Earth. It shows the energy emitted at each wavelength (and frequency). Use the information in the table to answer the following questions.

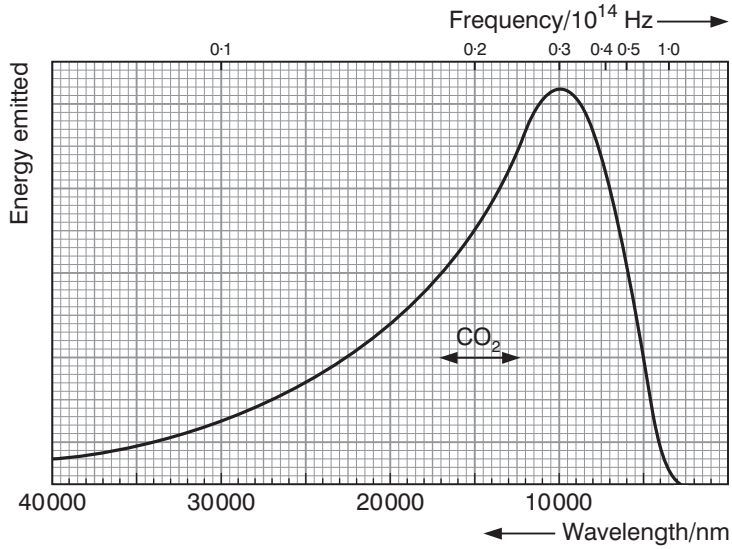


Figure 1 Infrared radiation emitted by the Earth

a The range of wavelengths absorbed by CO_2 in the atmosphere is shown in Figure 1. Mark on the Earth's radiation spectrum the absorption ranges (if any) of other gases that occur naturally in the atmosphere in considerable quantities: N_2, O_2, H_2O. (It is easier to use the wavelength ranges rather than the frequency ranges.)

b Which of these four *naturally abundant* gases are likely to have a greenhouse effect?

c What range of wavelengths of infrared radiation will be able to escape from Earth without absorption by these natural greenhouse gases? This range of frequencies acts as a '*window*' which keeps the Earth cool by allowing radiation to escape.

d Now look at the other gases in the table: CH_4, N_2O, CCl_3F and O_3.
- **i** Which are produced naturally?
- **ii** Which are produced as a result of human activities?

e Mark on the spectrum the absorption ranges of each of the gases mentioned in **d**.
- **i** Which are greenhouse gases?
- **ii** Which absorb radiation in the 'window' mentioned in **c**?

f From the information given, it is not possible to compare the *magnitude* of the different gases' greenhouse effects. What further information would you need in order to do this?

A8.1

The effect of concentration changes on chemical equilibria

In this activity you will carry out some quick test-tube reactions to investigate the effect of changing the concentration of a substance in an equilibrium mixture.

Requirements

- test-tubes and rack
- potassium chromate(VI) solution, 0.1 mol dm^{-3} (2 cm^3)
- protective gloves
- dilute sulphuric acid, 1.0 mol dm^{-3} (2 cm^3)
- dilute sodium hydroxide solution, 2.0 mol dm^{-3} (2 cm^3)
- teat pipettes
- distilled water
- potassium (or ammonium) thiocyanate solution KSCN (or NH_4SCN), 0.5 mol dm^{-3} (2 drops)
- iron(III) chloride solution, 0.5 mol dm^{-3} (2 drops)
- solid ammonium chloride (1 spatula load)
- glass stirring rod

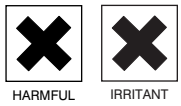
CARE Chromates(VI) irritate the skin and are suspected carcinogens. Avoid all skin contact. Any spillage should be washed off at once. Wear protective gloves.

CARE Thiocyanates and ammonium chloride are harmful.

ammonium chloride

dilute sulphuric acid

potassium chromate(VI) solution



potassium thiocyanate solution

sodium hydroxide solution

CARE Eye protection and gloves must be worn.

Introduction

The two equilibria in this activity involve coloured ions, so you can use the colour of the solution to investigate how the position of equilibrium changes when the concentration of one of the reactants is increased or decreased.

Equilibrium 1

Potassium chromate(VI) solution contains yellow chromate(VI) ions. In acidic solution, orange dichromate(VI) ions are formed.

$$\underset{\substack{\textit{chromate(VI) ion}\\ \text{yellow}}}{2CrO_4^{2-}(aq)} + 2H^+(aq) \rightleftharpoons \underset{\substack{\textit{dichromate(VI) ion}\\ \text{orange}}}{Cr_2O_7^{2-}(aq)} + H_2O(l)$$

1 Place 2 cm^3 potassium chromate(VI) solution (0.1 mol dm^{-3}) in a test-tube. (**CARE** Chromates(VI) irritate the skin and are suspected carcinogens. Avoid all skin contact. Wear gloves.)

2 Add dilute sulphuric acid (**CARE** Irritant) drop by drop, with gentle shaking, until there is no further colour change.

3 Now add dilute sodium hydroxide solution (**CARE** Corrosive) drop by drop, with gentle shaking, until there is no further colour change. (Hydroxide ions, $OH^-(aq)$, remove $H^+(aq)$ ions from the solution.)

4 Repeat steps **2** and **3**, and then record your observations in Table 1. Suggest a cause for each colour change (in terms of the concentration of the coloured ions) and then say what this tells you about the change in the position of equilibrium.

Change	Observation	Cause	What has happened to the position of equilibrium?
concentration $H^+(aq)$ increased			
concentration $H^+(aq)$ decreased			

Table 1

QUESTION

a Write an ionic equation to show how hydroxide ions, $OH^-(aq)$, remove $H^+(aq)$ ions from the solution. What *type* of reaction is this?

Equilibrium 2

Iron(III) ions and thiocyanate ions react in solution to produce a blood-red compound:

$$\underset{\textit{iron(III) ion}}{Fe^{3+}(aq)} + \underset{\textit{thiocyanate ion}}{SCN^-(aq)} \rightleftharpoons [FeSCN]^{2+}(aq)$$

pale yellow colourless blood red

5 Mix together 1 drop of iron(III) chloride solution ($0.5\,mol\,dm^{-3}$) and 1 drop of potassium thiocyanate solution ($0.5\,mol\,dm^{-3}$) in a test-tube, and add about $5\,cm^3$ of distilled water to form a pale orange-brown solution.

6 Divide this solution into four equal parts in four test-tubes.

7 Add 1 drop of iron(III) chloride solution to one test-tube, and 1 drop of potassium thiocyanate solution to a second. Compare the colours of these solutions with the two remaining tubes. Enter your observations in Table 2.

8 Add a spatula-load of solid ammonium chloride to a third test-tube and stir well. (The effect of this is to reduce the concentration of iron(III) ions in the solution. The chloride ions in ammonium chloride react with the $Fe^{3+}(aq)$ ions to produce $[FeCl_4]^-$ ions.) Compare the colour of this solution with the remaining tube and note your observation. Now complete the rest of Table 2.

Change	Observation	Cause	What has happened to the position of equilibrium?
concentration $Fe^{3+}(aq)$ increased			
concentration $SCN^-(aq)$ increased			
concentration $Fe^{3+}(aq)$ decreased			

Table 2

QUESTION

b How would the position of equilibrium be affected by increasing the concentration of $[FeSCN]^{2+}(aq)$ ions?

SUMMARY

c How does changing the concentration of one of the substances in an equilibrium mixture affect the position of equilibrium? Write a short paragraph to summarise your findings.

A8.2

Measuring the concentration of carbon dioxide in air samples

In this activity you will see how pH measurements can be used to find the concentration of carbon dioxide in samples of air. You will then consider the limitations of the method.

Introduction

To understand this activity you need to know what is meant by the pH of a solution. You will learn about this in more detail in **The Oceans**. For now it is sufficient to known the following.

The pH scale is a measure of the acidity or alkalinity of a solution. Pure water has pH = 7. Solutions with pH<7 are acidic; solutions with pH>7 are alkaline.

The pH scale represents the concentration of $H^+(aq)$ ions in a solution on a *logarithmic scale*. This means that a *tenfold* change in the concentration of $H^+(aq)$ ions is needed to produce a pH change of 1.

This is shown in Figure 1, which gives the hydrogen ion concentrations, $[H^+(aq)]$, corresponding to some pH numbers.

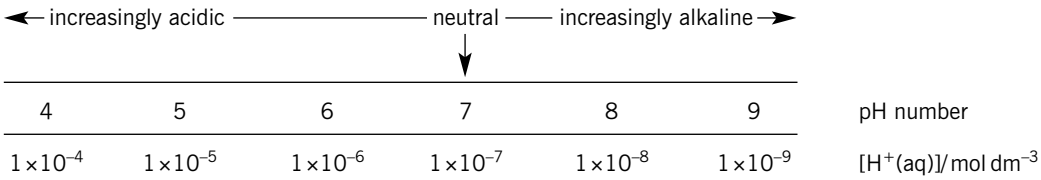


Figure 1 The pH scale

If the concentration of $H^+(aq)$ ions in a solution is halved, the pH only changes by 0.3.

Using pH to measure CO_2 concentration in air

Carbon dioxide is a weakly acidic gas, and this property can be used to measure the concentration of carbon dioxide in samples of air.

The carbon dioxide in an air sample is allowed to dissolve in water. Then the acidity of the water is measured. The greater the carbon dioxide concentration in the air sample, the more acidic the water will be. Here are the important reactions:

$$CO_2(g) + aq \rightleftharpoons CO_2(aq)$$
$$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

However, changes in the concentration of dissolved carbon dioxide lead to only small changes in the pH of the solution.

If a solution of sodium hydrogencarbonate is used in place of water, the pH of the solution also changes with the concentration of carbon dioxide in the air sample, but the changes in pH are larger, so that the method becomes much more sensitive.

A pump is used to bubble air through a solution of sodium hydrogencarbonate until equilibrium is reached (about 20 minutes). The air can be drawn from different sources for comparison (eg outdoors and indoors). Some sample results are shown in Table 1.

Sample	pH
Outdoor air	9.3
Indoor air	8.7
Carbon dioxide	5.9

Table 1 Sample results (bubbling the gas into the solution for 20 minutes)

The calibration graph (Figure 2) allows you to relate the pH of the sodium hydrogencarbonate solution to the concentration of carbon dioxide in the air sample.

(Biologists frequently use this technique to measure carbon dioxide concentrations in air samples. Instead of using a pH meter, they often use *bicarbonate indicator*. This is a standard solution of sodium hydrogencarbonate containing a mixture of indicators. These change colour according to the pH of the solution.)

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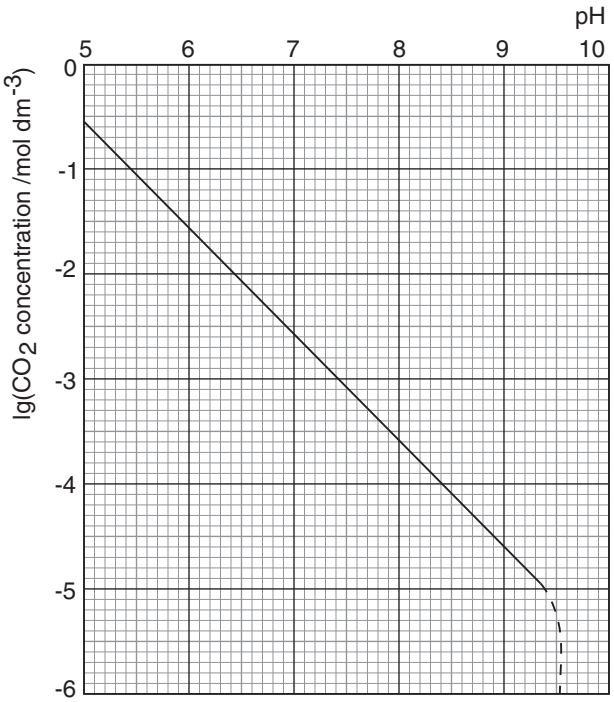


Figure 2 Calibration graph relating pH of the sodium hydrogencarbonate solution to the logarithm of the concentration of carbon dioxide in the air sample

QUESTIONS

a Use the sample results and the calibration graph to calculate the concentration of gaseous carbon dioxide in each sample. (Assume that equilibrium has been reached between the sample and the solution.)

b What is the uncertainty associated with a pH value which is read to 0.1 pH units? Calculate the percentage error for each of the pH values in the sample results.

c A difference of 0.1 pH units produces quite large differences after using the calibration graph and calculating the concentration

eg pH 9.0 gives a concentration of 2.5×10^{-5} mol dm^{-3}
but pH 8.9 gives a concentration of 3.6×10^{-5} mol dm^{-3}

What would be the percentage difference in the concentration calculated if the correct reading was pH 9.0 but the recorded value was 8.9?

d Is this method sensitive and accurate enough to detect the difference in carbon dioxide concentration between:
- **i** normal air and carbon dioxide gas?
- **ii** air outside and inside the laboratory?

e Comment on the limitations of this method as a way of finding the concentration of carbon dioxide in the atmosphere. How useful would the method be for chemists monitoring pollution of the atmosphere?

f Your results for the concentration of carbon dioxide in the air samples are in mol dm^{-3}. The more usual measure of gaseous concentration is percentage by volume. Convert your results into percentage by volume. (Assume that at room temperature and pressure 1 mole of carbon dioxide occupies 24 dm^3.)

A9

Controlling carbon dioxide

Reducing the rate of increase of carbon dioxide in the atmosphere is one of the greatest challenges for the world as we move into the 21st century. In this activity you will write a report using information from a variety of sources and try your hand at writing an abstract which summarises the content of your report.

Introduction

Carbon dioxide is the greenhouse gas causing most concern. Increased carbon dioxide emissions could upset the existing balance in the atmosphere.

Below, four possible approaches to the control and reduction of atmospheric carbon dioxide are outlined:

Approach 1 Choose the right fuel.
Approach 2 Economise on the use of energy in general.
Approach 3 Dispose of the carbon dioxide.
Approach 4 Encourage photosynthesis.

Your teacher will probably tell you which of these approaches to work on, but first answer the questions below.

Table 1 gives details of four possible fuels.

Fuel	Typical constituent	Standard enthalpy change of combustion of typical constituent/kJ mol^{-1}
coal	carbon	–394
natural gas	methane, CH_4	–890
gasoline	octane, C_8H_{18}	–5470
hydrogen	hydrogen, H_2	–286

Table 1 Four possible fuels

a For each fuel in Table 1, write an equation to represent its combustion.
b For each fuel, calculate the amount in moles of carbon dioxide given out per kJ of energy released by the fuel.
c What are the implications of your answers?

What you do

1 Write a report of no more than 400 words on *one* of the four approaches. Refer to the statistics on the **Information Sheet** (*World resources and the consumption of energy*) as appropriate, and use any other sources of information you can find. (These may be Salters Advanced Chemistry units, textbooks, articles or the Internet.) At the end of your report, list clearly any additional sources you have used. (This list is not included in the word count.) You should refer to this list in your report where appropriate. For example, where you have copied material directly from another source, this must be indicated in the text and the source properly acknowledged.

You may be asked to make an oral presentation to the class on your approach.

2 In the second part of this activity, a person is chosen to present a short briefing to the class on each of the approaches. After all four briefings have been presented, the class can work together to discuss an overall approach – which might be a combination of some or all of the four.

The overall objective is to recommend a strategy for bringing about a substantial reduction in the amount of carbon dioxide emitted into the atmosphere throughout the world.

The scale of the problem

When tackling this activity, you must be aware of the scale of the problem. It is enormous, because the amount of fossil fuel burned throughout the world is now huge: about 30 thousand million tonnes (30 Gt) of carbon dioxide are released into the atmosphere each year from human activities. The problem is much too big for a quick, easy solution.

You should also be aware of the scale of natural processes involving carbon dioxide compared with the scale of carbon dioxide production by humans. To remind yourself, have a look at the diagram of the global carbon cycle in **Storyline A8**.

Approach 1: Choose the right fuel

Some fossil fuels give out more carbon dioxide than others when they burn.

Prepare a report on the control of carbon dioxide by selective use of fuels. You should decide which fuels are preferable for which uses. You should indicate any problems and drawbacks involved in this approach.

Bear in mind the following points:

- Your scheme will have to take account of the available reserves of the fuels concerned.
- Different fuels are appropriate for different uses. For example, most forms of transport need liquid fuels.
- Electricity generation is a major use of fossil fuels.
- Hydrogen is a possible fuel that may have attractions, but hydrogen does not occur naturally: it has to be manufactured.

You might also consider the implications of using fuels derived from biomass (eg ethanol produced from grain or from wood) rather than those from fossil fuels.

Approach 2: Economise on the use of energy in general

All fossil fuels release carbon dioxide when they burn. Economising on the use of energy in general will reduce consumption of fossil fuels, and so reduce carbon dioxide emission. Energy consumption can also be reduced by increasing the efficiency of energy conversions, particularly in power stations and motor vehicle engines.

Prepare a report on the control of carbon dioxide by economising on the use of energy worldwide. You should make suggestions concerning how this could be done. You should indicate any problems and drawbacks involved in this approach. Try to find information about some of the techniques for increasing fuel efficiency, for example fluidised bed combustion in power stations.

Bear in mind the following points:

- Standard of living is closely related to energy consumption (but see the next point).
- There are examples, over the last 30–40 years, of energy economy and efficiency drives in Western countries. These have led to a reduction in the use of fossil fuels without causing a significant fall in standard of living.
- Electricity generation is a major use of fossil fuels.
- You may want to consider alternative energy sources. Nuclear energy may have attractions in this context, but bear in mind that it carries with it a number of environmental hazards.

Approach 3: Dispose of the carbon dioxide

It might be possible to get rid of carbon dioxide, after it has been formed but before it can escape into the atmosphere. The problem with this approach is the enormous quantity of carbon dioxide involved: 30 thousand million tonnes each year.

Carbon dioxide removal is not yet a practical possibility on a large scale, though a number of methods have been suggested. One possibility is to use a special solvent in which carbon dioxide is highly soluble. Exhaust gases from a power station would be passed through the solvent so that the carbon dioxide dissolved. The solvent would then be heated to expel the carbon dioxide. The solvent would be recycled.

The carbon dioxide expelled from the solvent would then have to be disposed of. The question is, where? It could in theory be liquefied and pumped to a depth of more than 500 metres beneath the sea. At this depth the pressure is so great that the carbon dioxide would remain at the bottom as a liquid. Another possibility would be to dump the carbon dioxide underground in spent oil or gas wells from which all the oil or gas had been removed.

The technology for this kind of process is expensive. It might double the capital cost of a small coal-fired power station, and it could raise the price of electricity by about 75%.

Prepare a report on the control of carbon dioxide by disposing of the gas. You should indicate the advantages of this approach and mention any problems and drawbacks involved. If you can invent other possible ways of absorbing and disposing of carbon dioxide, you could mention these too.

Approach 4: Encourage photosynthesis

Photosynthesis removes carbon dioxide from the atmosphere, converting it to carbohydrate and oxygen.

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

Worldwide, about 500 Gt of carbon dioxide are removed by photosynthesis each year: compare this with the 30 Gt produced from the combustion of fossil fuels.

Increasing the rate of global photosynthesis will help remove carbon dioxide from the atmosphere. Photosynthesis occurs particularly rapidly in the rain forests of the tropics. However, the rain forests are being destroyed at a great rate by human activities. What is more, destroying the forests actually adds more carbon dioxide to the atmosphere when the wood is burned or decays. It is estimated that about 2 Gt of carbon dioxide per year are released due to the destruction of forests around the world.

At present, photosynthesis can only be carried out by plants. But a great deal of research is going on to try and find out the exact mechanism by which photosynthesis works. Once this is understood, it may be possible to arrange for photosynthesis to occur in artificial systems, outside plants. There might then be the possibility of using artificial photosynthesis to absorb atmospheric carbon dioxide and at the same time produce carbohydrates for food or fuels.

Prepare a report on the control of carbon dioxide by encouraging photosynthesis. You should indicate the advantages of this approach and mention any problems and drawbacks involved. If you can think of other possible ways of making use of photosynthesis, you could mention these too.

Information Sheet: World resources and the consumption of energy

Energy source	Consumption /million tonnes of oil equivalent*
oil	3389
natural gas	2016
coal	2219
hydroelectric	226
nuclear	627
total	8477

*Table 1 World consumption of different energy sources, 1998 (*BP Amoco *Statistical Review of World Energy, 1999)*

Fuel	Reserves /million tonnes of oil equivalent*
oil	143 000
natural gas	134 000
coal	656 000
total	963 000

*Table 2 Estimated world reserves of fossil fuels, 1998 (*BP Amoco *Statistical Review of World Energy, 1999)*

	Consumption/million tonnes of oil equivalent*					
Region	Oil	Gas	Coal	Hydro	Nuclear	Total
North America	1008	647	566	57	204	2492
South and Central America	217	77	19	45	3	361
Europe	760	385	351	50	243	1788
Former Soviet Union	184	746	167	20	50	897
China	190	17	615	17	4	843
Japan	255	63	88	9	84	499
Africa	112	44	96	6	4	262

*Table 3 Energy consumption in different regions of the world, 1998 (*BP Amoco *Statistical Review of World Energy, 1999)*

Fuel	Percentage of generated electricity
coal	38.4
oil	9.3
gas	14.8
nuclear	17.7
hydroelectric	18.4
other (inc. geothermal, solar)	1.4

Table 4 Percentage of the electricity generated from different fuels worldwide in 1996 (Key World Energy Statistics, IEA, 1998*)*

Fuel	Percentage of fuel consumed
coal	24.0
oil	35.3
gas	20.2
nuclear	6.7
hydroelectric	2.3
combustible residues and waste	11.1
other (inc. geothermal, solar)	0.4

Table 5 World fuel consumption in 1996 (Key World Energy Statistics, IEA, 1998*)*

* So that there can be an easy comparison between fuels, the consumption is calculated in terms of the energy generated by oil: one tonne of oil equivalent equals 42 GJ or, for example, 1.5 tonnes of hard coal. It produces 12 MW hr of electricity in a modern power station.

A10

Check your notes on *The Atmosphere*

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

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

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

- The gases present in the atmosphere, including some major pollutants; understand values for composition by volume measured in percentage concentration and in parts per million (ppm) (**Storyline A1**).
- The idea that rotational, vibrational and electronic energies are quantised.
- The qualitative changes in rotational, vibrational and electronic energy of molecules caused by the absorption of radiation of appropriate frequency.
- The relationship between frequency and energy of electromagnetic radiation.
- The structure and reactivity of ozone and the way it is formed and destroyed in the stratosphere; how ozone acts as a sunscreen (**Storyline A3**; **Activity A3.1**).
- The factors that affect the rate of a chemical reaction and the use of collision theory to explain the effects.
- The meaning of the terms: *enthalpy profile* and *activation enthalpy*.
- The use of the concept of activation enthalpy to explain the qualitative effect of temperature changes on rate of reaction.
- The role of catalysts in providing alternative routes of lower activation enthalpy; homogeneous catalysis in terms of the formation of intermediates.
- The difference between homolytic and heterolytic fission of a covalent bond.
- The formation, nature and reactivity of radicals; the mechanism of a radical chain-reaction involving initiation, propagation and termination.
- The reaction of alkanes with halogens (**Activities A3.2** and **A3.3**).
- The nature and names of halogenoalkanes.
- The meaning of the terms: *hydrolysis*, *substitution*, *nucleophile* and *carbocation*.
- Outline of the preparation of a halogenoalkane from an alcohol and the principle stages in the purification of an organic liquid product (**Activity A4.2**).
- The characteristic properties of halogenoalkanes, comparing fluoro-, chloro-, bromo- and iodo-compounds: boiling points, formation of radicals by interaction with ultraviolet radiation (**Storyline A3**), and nucleophilic substitution with water, hydroxide ions and ammonia.
- The mechanism of nucleophilic substitution in halogenoalkanes.
- The use of relative electronegativity values to predict bond polarity in a covalent bond; the relationship between reactivity of halogenoalkenes and bond enthalpy and bond polarity.
- The nature and uses of chlorofluorocarbons (CFCs) (**Storyline A4**) and the relative advantages and disadvantages of replacement compounds (**Activity A4.3**).
- The chemical basis of the depletion of ozone in the stratosphere due to halogenoalkanes, involving the formation of halogen atoms and the catalytic role of these atoms in ozone destruction (**Storyline A3**).
- The relationship between the 'greenhouse effect' in the troposphere and the absorption characteristics of atmospheric gases (**Storyline A6** and **A7**; **Activity A6**).
- A comparison of the different approaches to the control of global warming through the control of carbon dioxide emissions (**Storyline A9; Activity A9**).
- The meaning of the term: *dynamic equilibrium*.
- The physical and chemical changes occurring when carbon dioxide dissolves in water, and the associated equilibria.
- The use of Le Chatelier's Principle to explain and predict the effects on the position of equilibrium of changes in concentration, temperature and pressure.

PRI

Some important polymers: introductory data

This activity is part of the introduction to the unit. It will help your data-analysis and information-retrieval skills. After carrying out the activity you should be familiar with the names of some important polymers. You will find out how much of each is produced and what the major uses are.

Polymers are a major product of the chemical industry. About 60% of all the chemicals it produces are used to make polymer products. It is now difficult to imagine life without them.

Polymers are used to make a range of different types of products (Figure 1). Some polymers are more suited to one particular application than to others. You will learn later in the unit how the structure of a polymer affects its properties and its use. The processing of a polymer is very important, too. It can determine the way chains pack together, which affects the properties of the polymer.

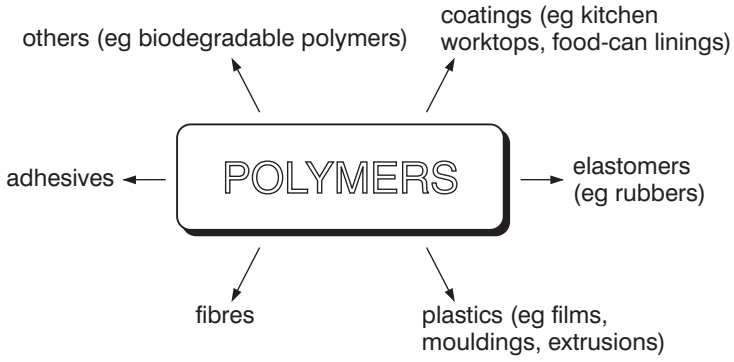


Figure 1 Some uses of polymers

You will meet examples of 'performance' polymers for use in special situations – polymers that shine in the dark, heat-resistant polymers, biodegradable polymers. These form an exciting new generation of polymers that are being developed in the 21st century.

By far the largest percentage of polymer production is concerned with making plastics for packaging, containers, tubes and piping.

Moulding of polymers
The polymer is often in the form of pellets. When heated these become soft and can be pushed through nozzles to form **pipes** (for example, for drainage) and **tubes** (for wires and cables). They can also be pushed through nozzles into moulds, where they cool to form the desired shape (buckets, bowls, boxes). This is known as **injection moulding**. In **blow moulding**, air is blown into the mould to form bottles. The molten polymer can also be extruded as film (shrink wrap, bags, bin liners).

This activity is concerned with the uses of some of the more common addition polymers. You will be asked to note the formula of each polymer and the formula of the monomer it is made from. But later in the unit you will learn more about how polymers are made and how their properties and uses are related to their structures.

Figures 2–6 give the annual UK production and uses of the polymers, together with the world production. (You may wish to colour the sectors of the pie charts.)

Poly(ethene)

There are three main forms of poly(ethene). One is called high density poly(ethene), hdpe, and another is low density poly(ethene), ldpe. These are discussed in this unit. The third form, linear low density poly(ethene), lldpe, is discussed in a later unit, **Designer Polymers**.

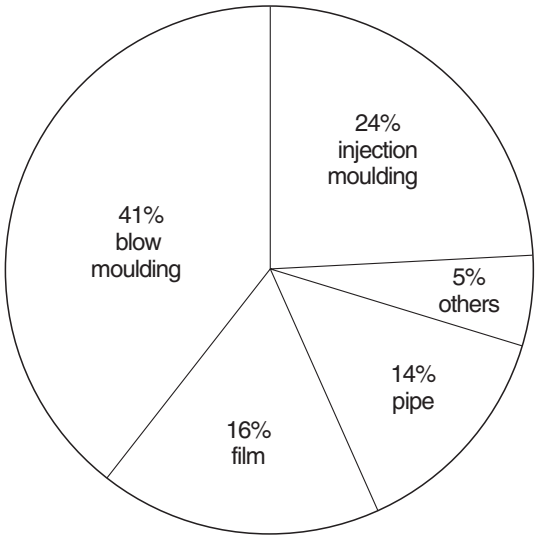


Figure 2 Uses of hdpe (high density poly(ethene))

Annual production of poly(ethene)		
UK	hdpe	280 000 tonnes
	lldpe	160 000 tonnes
	ldpe	200 000 tonnes
World	hdpe	22.5 million tonnes
	lldpe	14 million tonnes
	ldpe	15.6 million tonnes

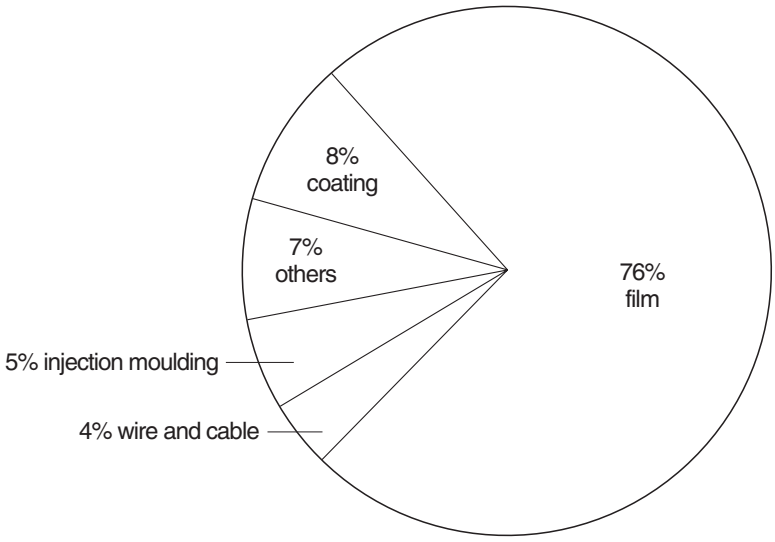


Figure 3 Uses of ldpe / lldpe (low density and linear low density poly(ethene))

Poly(propene)

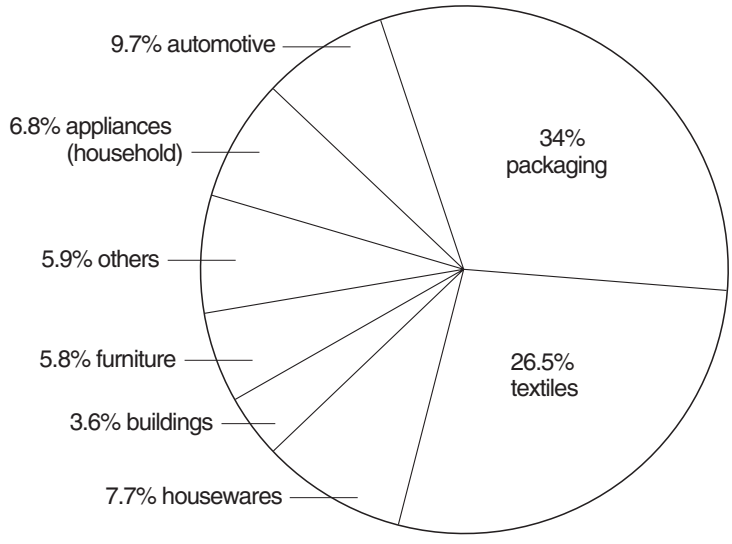


Figure 4 Uses of poly(propene)

Annual production of poly(propene)	
UK	300 000 tonnes
World	23.5 million tonnes

Poly(chloroethene) (polyvinyl chloride, PVC)

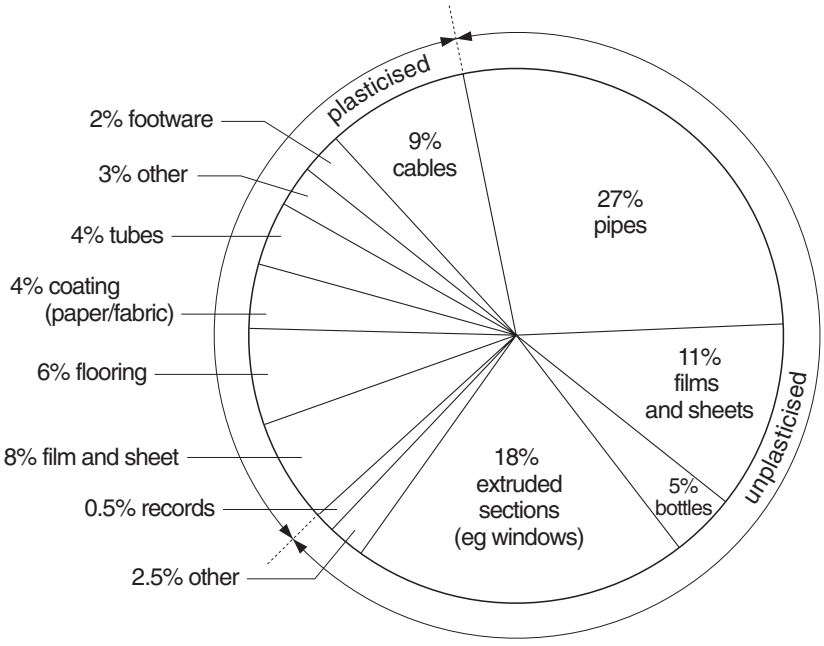


Figure 5 Uses of PVC

Annual production of PVC	
UK	470 000 tonnes
World	27 million tonnes

Poly(phenylethene) (polystyrene)

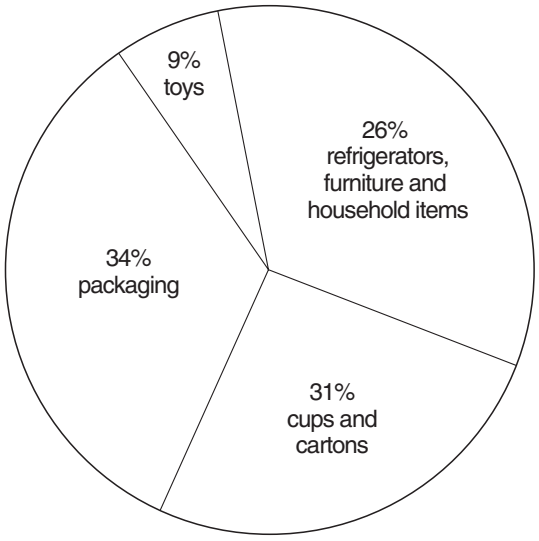


Figure 6 Uses of polystyrene

Annual production of polystyrene	
UK	270 000 tonnes
World	8.5 million tonnes

QUESTIONS

a Draw a table, like the one below, for the above polymers and complete as much of it as possible. You may not be able to give the formulae of the polymers at this stage but you will be able to later in the unit.

Name of polymer	Formula of monomer	Formula of polymer	Main uses

b Use a computer to produce a bar chart comparing the UK production and world production of these polymers. Use the data above and any further information that you can find on the Internet (start your search at the Salters Advanced Chemistry web site).

i In what ways can you relate the differences in production to the different products made from the five polymers?

ii What are the major differences between the uses of the high density and low density forms of poly(ethene)?

iii Poly(propene) is often said to be similar in use to hdpe. In what respects is this true? What is the major difference in the uses of the two polymers?

PR2

Making poly(phenylethene) (Optional extension)

In this activity you will use a peroxide to initiate the addition polymerisation of an alkene. Phenylethene is a convenient alkene to use because it is a liquid with a boiling point of 145 °C. Di(dodecanoyl) peroxide (or lauroyl peroxide) is the initiator.

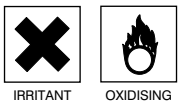
Requirements

- phenylethene (styrene) (10 cm^3)
- 10 cm^3 measuring cylinder
- di(dodecanoyl) peroxide (0.2 g)
- boiling tube and 2 test-tubes
- 250 cm^3 beaker
- cottonwool
- source of hot water
- methylbenzene (5 cm^3)
- bromine water (2 cm^3)
- spatula
- access to balance
- access to fume cupboard

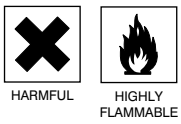
CARE You should carry out this experiment in a fume cupboard.

bromine water

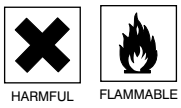
di(dodecanoyl) peroxide



methylbenzene



phenylethene (styrene)



CARE Eye protection must be worn.

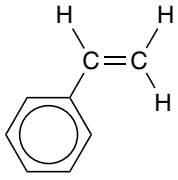
What you do

1. Place 10 cm^3 of phenylethene in a boiling tube. (**CARE** Phenylethene is flammable and harmful. Avoid breathing the vapour.)
2. Add about 0.2 g of di(dodecanoyl) peroxide (**CARE** Irritant) and shake the tube until the solid has dissolved.
3. Plug the tube with cottonwool and then heat it in a beaker of boiling water *in a fume cupboard* for about 20 minutes.
4. Compare the contents of the tube with the original phenylethene. Is there evidence that polymerisation is taking place?
5. Leave the tube in an oven or water bath at about 50 °C until the contents have set. (After step **3** you can pour the contents into a mould and use that instead of the boiling tube if you prefer.)
6. Dissolve a small quantity of the solid formed in methylbenzene. Add a few drops of the solution to 1 cm^3 bromine water in a test-tube. Stopper the tube and shake.
7. Now add a few drops of the monomer, phenylethene, to 1 cm^3 bromine water in a separate test-tube. Stopper the tube and shake.
8. Make a record of your observations.

QUESTIONS

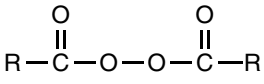
a What do your observations in steps **6** and **7** tell you about the structures of the monomer and the resulting polymer?

b The structure of phenylethene is:



Draw out part of the structure of poly(phenylethene).

c Di(dodecanoyl) peroxide is:



where R is a $CH_3(CH_2)_{10}$ group. Explain how this compound acts as an initiator for the polymerisation.

PR3

Using spaghetti to model polymer structure

In this activity, you will use strands of spaghetti to model how the molecules of some polymers are aligned in a solid

Requirements

- spaghetti (about 250 g)
- 2 dm^3 beaker (or saucepan)
- Bunsen burner, tripod and gauze (or kitchen hob)
- transparent container with a flat base and straight sides (such as a plastic ice cream or sandwich box)
- strainer

CARE Do not eat any spaghetti cooked in the laboratory.

What you do

1 Cook some spaghetti, in a saucepan or large beaker, using the manufacturer's instructions for the amount of water and length of time.
2 When cooked, strain the spaghetti so that it is free of water and pour it into the container.
3 Allow it to cool.
4 Turn out the solid cake. Sketch the arrangement of spaghetti strands on the base of the solid cake.

The spaghetti acts as a model for the chains in a polymer and the way they pack together in solid materials.

5 Label on your diagram:
i areas where the arrangement resembles a crystalline structure
ii areas where the arrangement resembles an amorphous structure.

QUESTION

Does the spaghetti model resemble a syntactic or an atactic polymer? Explain your answer.

PR5.I

Deflecting jets

This experiment illustrates the section in* Chemical Ideas 5.3 *which is about bond polarity and dipole moments. You are going to test streams of different liquids to see whether they are affected by an electrically-charged rod. If the molecules in the liquid are polar they should be attracted towards the rod.

Requirements

- burettes (5)
- water (50 cm^3)
- propanone (50 cm^3)
- ethanol (50 cm^3)
- cyclohexane (50 cm^3)
- methylbenzene (50 cm^3)
- 250 cm^3 beakers (5)
- plastic rulers (5)
- protective gloves

CARE Most of the liquids used are flammable. There must be no naked flames in the laboratory while doing this experiment.

WARNING Some of the liquids may dissolve plastic, so do not let them come into contact with the ruler.

WARNING At the end of the activity the liquids must be disposed of properly, as directed by your teacher. Do not throw any liquid other than water down the sink.

cyclohexane — HIGHLY FLAMMABLE

ethanol — HIGHLY FLAMMABLE

methylbenzene — HARMFUL; HIGHLY FLAMMABLE

propanone — HIGHLY FLAMMABLE

CARE Eye protection and disposable gloves must be worn. — WEAR EYE PROTECTION; WEAR PROTECTIVE GLOVES

What you do

1 Set up a burette and fill it with one of the liquids provided. (**CARE** Some of these liquids are flammable and some have harmful vapours. Take notice of the hazard warnings associated with each liquid.) To save time, each group should start with a different liquid and the groups should move from burette to burette during the experiment.

2 Place an empty 250 cm^3 beaker under the burette to catch the jet of liquid. You can refill the burette from the beaker at the end of your turn.

3 Charge the ruler by rubbing it vigorously with a piece of dry cloth. A woollen sweater is good for this. Then turn on the burette tap so that a jet of liquid flows into the beaker.

4 Bring the ruler towards the jet *but do not let them touch* (see Figure 1). Observe what happens. Record how much, if at all, the jet of liquid is deflected, and what this tells you about the structure of the molecule. (Note that the charged rod can set up *induced* dipoles in the molecules of the liquid and lead to small deflections with molecules which possess no *permanent* dipole. So even molecules with no permanent dipole can give small deflections.)

5 Repeat the experiment with the other liquids provided.

6 Make out a table like the one that follows, and record your results.

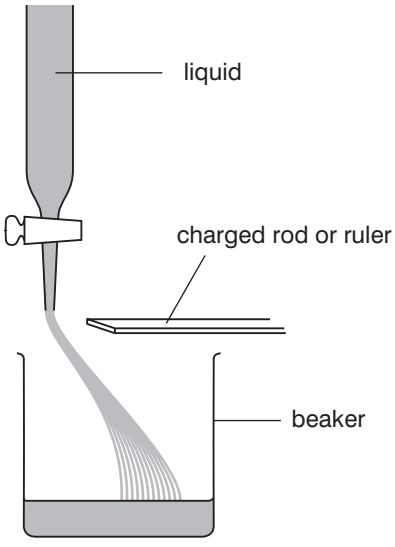


Figure 1 Deflecting jets of liquids

Liquid	Structure	Effect of charged rod on jet of liquid	Does the molecule possess a permanent dipole?
ethanol	C_2H_5OH		

QUESTIONS

a Which liquids contain molecules that possess dipoles?

b Which groups of atoms in these molecules are responsible for the polarity?

PR5.2

Viscosity in alcohols

This activity requires you to interpret experimental observations in terms of the ideas on intermolecular forces you have been reading about.

Requirements

- test-tubes (3)
- stoppers (3)
- propan-1-ol (10 cm^3)
- propane-1,2-diol (10 cm^3)
- propane-1,2,3-triol (10 cm^3)
- stopclock

CARE Propan-1-ol and propane-1,2-diol are flammable. Keep well away from naked flames.

propan-1-ol

HIGHLY FLAMMABLE

propane-1,2-diol

HIGHLY FLAMMABLE

CARE Eye protection must be worn.

WEAR EYE PROTECTION

What you do

1 Pour some propan-1-ol into a test-tube so that when it is stoppered there will be a small air gap left at the top of the liquid.
2 Invert the tube and record the time the bubble takes to rise through the liquid.
3 Repeat for the other two alcohols, using the other two test-tubes.

QUESTIONS

Viscosity (how thick or syrupy a liquid is) is a measure of how strongly the molecules attract each other. In this activity, the molecules must be forced apart to allow the bubble to rise.

a Draw structural formulae for the three alcohols you have used.

b Explain your results in terms of the groups contained in the alcohol molecules and the interactions between them.

PR5.3

Now you see it ...

Poly(ethenol) is used to make plastic laundry bags for use in hospitals. The bags dissolve during the washing, which means that hospital workers do not need to handle the dirty linen and run the risk of infection. This activity introduces you to poly(ethenol), and gives you an opportunity to plan and carry out an investigation.

Requirements

- poly(ethenol) film (hot-water soluble variety – several small pieces)
- 250 cm^3 beaker
- washing powder
- glass rod
- Bunsen burner, tripod and gauze
- thermometer

CARE Eye protection must be worn.

WEAR EYE PROTECTION

What you do

Plan and carry out an investigation to find out how fast poly(ethenol) film dissolves in water under different conditions such as might be present in a washing machine.

What recommendations would you make to hospitals about the length of the wash cycle and the temperature of the wash?

PR5.4

Making 'slime'

In this activity you will have the opportunity to prepare a novel material and examine its properties. You can then relate these properties to its structure.

Requirements

- polystyrene drinking cup
- sodium borate solution, 4% (10 cm^3)
- poly(ethenol) solution, 4% (50 cm^3)
- protective gloves
- wooden sticks for stirring (flat-sided ones work best)
- 50 cm^3 measuring cylinder
- 10 cm^3 measuring cylinder
- green food colouring or fluorescent dye (optional)

WARNING 'Slime' spoils carpets and can remove paint.

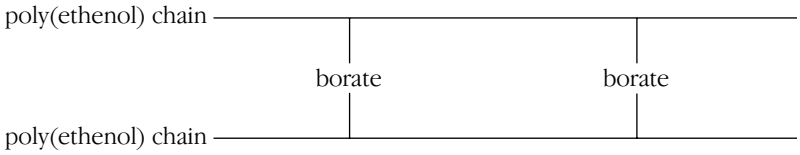
CARE Eye protection and gloves must be worn.

What you do

1. Put about 50 cm^3 of poly(ethenol) solution into the polystyrene cup. Stir the solution and note its appearance. (A few drops of food colouring or fluorescent dye may be added at this stage.)
2. Add 10 cm^3 of sodium borate solution and stir the mixture vigorously. Keep on stirring while the mixture is setting. When the mixture has set to a gel, remove it from the cup and continue to shape it with your hands (wear gloves).
3. Investigate the properties of the 'slime' you have produced and compare it with the poly(ethenol) solution you started with. 'Slime' is not dangerous, but as a precaution you should wear gloves and wash your hands at the end of the experiment.

Explanation

Borate ions in the sodium borate form cross-links between the poly(ethenol) chains:



The forces produced by these cross-links are of a different kind to the intermolecular forces between poly(ethenol) chains. They are also stronger, which allows you to see more clearly the effects of introducing forces between polymer molecules.

Summary

Write a brief account of the properties of 'slime' and describe how they differ from those of poly(ethenol). Explain your observations in terms of the intermolecular forces which are present.

PR5.5

The oxidation of alcohols

In this activity you investigate how different alcohols are affected by an acidified solution of potassiium dichromate (VI).

Requirements

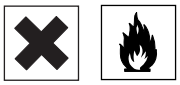
- potassium dichromate(VI) solution, 0.1 mol dm^{-3} (2 cm^3)
- dilute sulphuric acid, 2 mol dm^{-3} (5 cm^3)
- ethanol (3 drops)
- propan-1-ol (3 drops)
- butan-2-ol (3 drops)
- 2-methylpropan-2-ol (3 drops)
- test tubes and rack
- 250 cm^3 beaker
- a source of hot water

CARE 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 vapour.

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

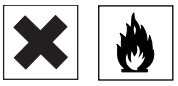
CARE Eye protection and gloves must be worn.

butan-2-ol



ethanol

2-methylpropan-2-ol



potassium dichromate(VI) solution

propan-1-ol

sulphuric acid

Comparing different alcohols

1 Place about 1 cm depth of 0.1 mol dm^{-3} potassium dichromate(VI) solution in a test-tube. Add 2 mol dm^{-3} sulphuric acid 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 this oxidising mixture on a range of alcohols, for example ethanol, propan-1-ol, butan-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.) Label the tube.

3 Repeat step **2** for all the alcohols, using a different tube for each alcohol.

4 Warm the mixtures by placing the tubes in a beaker of boiling water.

5 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.

QUESTIONS

a There is a pattern in the behaviour of the alcohols towards oxidation. Describe the pattern.

b There are three different structural types of alcohol in this investigation. Suggest why the three types behave differently. Building models of a series such as butan-1-ol, butan-2-ol and 2-methylpropan-2-ol might help you see more clearly what is happening.

PR6

Poly(pyrrole) – a conducting polymer

In this experiment you are going to 'grow' some poly(pyrrole) on a nickel electrode and then peel off the film of polymer so that you can test its conducting properties. You will only be able to peel the polymer off if the nickel electrode is very clean and smooth.

Requirements

- pyrrole (0.68 g)
- copper foil (1 cm wide strip)
- nickel spatula
- wire wool or emery cloth
- 'Brasso' metal polish
- small pieces of cloth
- paper towels
- sodium 4-methylbenzenesulphonate solution (p-toluenesulphonic acid sodium salt solution), 0.1 mol dm^{-3} (200 cm^3)
- 250 cm^3 beaker
- 250 cm^3 conical flask
- 0–4.7 kΩ variable resistor
- 12 V d.c. supply (in 2 V steps)
- ammeter to read 30 mA
- razor blades or equivalent
- teat pipette
- propanone (20 cm^3)
- crocodile clips
- wires
- microscope slides
- multimeter
- 1.5 V light bulb and holder
- access to fume cupboard

propanone

HIGHLY FLAMMABLE

pyrrole

HARMFUL IRRITANT FLAMMABLE

sodium 4-methylbenzenesulphonate solution

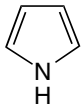
IRRITANT

CARE Eye protection must be worn.

WEAR EYE PROTECTION

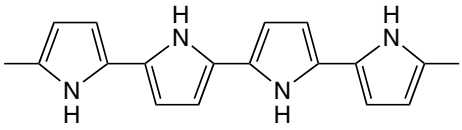
What is poly(pyrrole)?

The structure of pyrrole is:



It contains an unsaturated five-membered ring consisting of four carbon atoms and one nitrogen atom.

Poly(pyrrole) has this structure:



Part 1: Making poly(pyrrole)

1 The copper strip should be long enough to reach to the bottom of a 250 cm^3 beaker and also loop over the rim of the beaker at the top. This piece of copper will be one of your electrodes. Clean it with wire wool or emery cloth, and then rinse it with distilled water.

2 Use the flat end of a nickel spatula for the other electrode. Clean it with 'Brasso' (*not wire wool or emery cloth*). Rinse off the 'Brasso' with distilled water, then rinse the end of the spatula in propanone and dry it in the air.

3 Use a teat pipette to drip 0.34 g of pyrrole into a 250 cm^3 conical flask. (**CARE** Pyrrole is an irritant and has an unpleasant smell. Work in a fume cupboard and, if you spill any pyrrole on your hands, wash it off with lots of water.)

4 Add 100 cm^3 of 0.1 mol dm^{-3} sodium 4-methylbenzenesulphonate solution to the pyrrole. Carefully swirl the flask until the pyrrole has dissolved.

5 Pour the pyrrole solution into the 250 cm^3 beaker and set up the circuit illustrated in Figure 1.

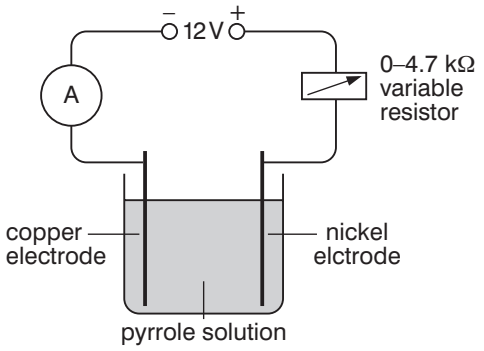


Figure 1 Making poly(pyrrole)

6 Start with the variable resistor at its maximum setting. Slowly increase the current by reducing the resistance until the ammeter reads 30 mA.

7 The nickel electrode should turn black within about 30 seconds. Bubbles of hydrogen will form at the copper electrode. Leave the experiment running for about 45 minutes in all.

8 Switch off the current and remove the nickel electrode. Wash it with water, then carefully peel off the poly(pyrrole) film. If you slide a razor blade between the film and the nickel you should be able to lift the intact film away from the electrode.

Keep the apparatus to use again in Part 3.

Part 2: Testing the conductivity of poly(pyrrole)

9 Support the polymer film on a microscope slide. It is best to fold the film in half and half again (four thicknesses). This reduces the chance of it burning out when a current is passed through it.

10 Use crocodile clips and wires to connect the polymer film into the circuit shown in Figure 2.

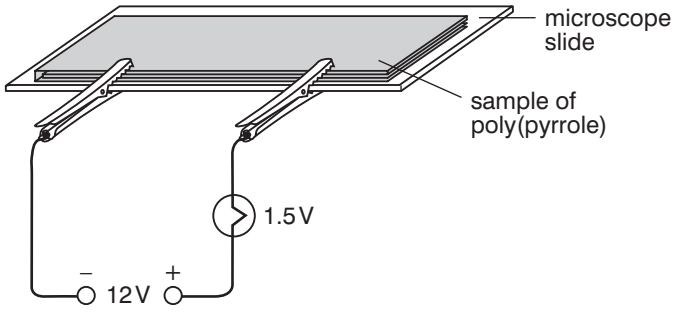


Figure 2 Testing the conductivity of poly(pyrrole)

11 First use the resistance setting on a multimeter to test whether the polymer has a measurable resistance. Then try to see whether you can make a 1.5 V bulb light with the poly(pyrrole) in the circuit. Do not put too high a voltage across the poly(pyrrole) or it may get hot and decompose. You should find that when the crocodile clips are about 1 cm apart the bulb will light at about 12 volts.

Part 3: Making a sample of poly(pyrrole) change colour

12 Using a clean nickel electrode, set up a fresh experiment to make poly(pyrrole). Start the experiment and watch it carefully. Switch it off as soon as the nickel electrode looks black. Take the electrode out of the electrolyte and examine its colour.

13 Put the coated nickel electrode back into the circuit. Reduce the voltage setting to 2 V and reverse the connections on the power supply so that the nickel strip becomes the negative electrode. Turn the power back on.

QUESTIONS

The poly(pyrrole) will gradually change colour. Take the electrode out of solution and examine its colour over a two-minute period.

a Is poly(pyrrole) as good a conductor as copper wire? How does the conductivity of poly(pyrrole) compare with polymers such as poly(ethene)?

b What colour is the poly(pyrrole) you made in the first experiment?

c Is it the same colour as the polymer film you made in step **12**?

d What colour was the poly(pyrrole) when it first came out of solution in step **13**?

e The poly(pyrrole) gains electrons at the negative electrode in step **13**. Has it been reduced or oxidised?

f Suggest why the poly(pyrrole) changes back to its original colour when it is exposed to air.

PR7

Check your notes on *The Polymer Revolution*

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

Use this list as the basis of a summary of the unit by collecting together the related points and arranging them in groups. Check that your notes cover the points and are organised in appropriate ways. Remember that you will be coming back to many of the ideas in later units. In particular you will use many of the ideas about properties and structure in the **Designer Polymers** unit.

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

- The historical development of addition polymers: discovery of poly(ethene) (**Storyline PR2**), different kinds of poly(ethene), Ziegler-Natta catalysts (**Storyline PR3**), conducting and light-emitting polymers (**Storyline PR6**) and dissolving polymers (**Storyline PR5**).
- Some examples of polymers discovered by accident (**Storyline** in general).
- Use of the terms: *polymer*, *repeating unit* and *monomer*.
- The meaning of the term: *addition polymerisation*.
- Predicting the structural formula of the addition polymer formed from given monomer(s), and vice versa.
- The use of systematic nomenclature to name alkenes.
- *Cis-trans* (geometric) isomers.
- The addition reactions of alkenes with the following: bromine, hydrogen bromide, hydrogen in the presence of a catalyst, and water in the presence of a catalyst.
- The meaning of the terms: *addition* and *electrophile*.
- The mechanism of the electrophilic addition reaction between bromine and alkenes.
- Whether a molecule is polar or non-polar is determined by its shape and the polarity of its bonds.
- Description and examples of the following types of intermolecular forces: instantaneous dipole–induced dipole attractions, permanent dipole–permanent dipole attractions and hydrogen bonding.
- The principal features of the molecular structure of water: bonding and shape of the water molecule and hydrogen bonding in water and ice.
- Explanation of the properties of addition polymers and other substances in terms of intermolecular attractions.
- The meaning of the terms: *thermoplastic*, *thermoset* and *co-polymer*.
- Crystallinity in polymers.
- The relationship between the properties of addition polymers and aspects of their molecular structure: chain length, side-groups, chain branching, chain flexibility, cross-linking and stereoregularity.
- The relationship of the properties of a dissolving polymer to its molecular structure (**Storyline PR5**).

WMI

The origins and development of the modern pharmaceutical industry

In this activity your class will divide into three groups. Each group will prepare a short presentation on one of the following topics.

1 Folklore in medicine
2 Medicine discovery and the nation's health
3 The British pharmaceutical industry

Finding information

You are expected to research your topic by searching the Internet. Start by looking at the Salters Advanced Chemistry web site which will link you to other sites which are relevant. Some suggestions for the focus of your research and how you might organise your presentation are given below for each topic.

1: Folklore in medicine

A suggested format for your presentation is a discussion between two people, one arguing the case based on your research, for traditional remedies, the other the case of someone who does not believe in folk medicine.

The case *against* might include some of the following points.

- We are civilised now: we don't believe in medicine men, voodoo and superstition.
- Most of these medicines work by 'the placebo effect' – people *believe* the medicines are going to make them better, so they do. Take away the primitive beliefs and the medicines won't work.
- In primitive communities it was kill or cure. Any medicine was better than none.

2: Medicine discovery and the nation's health

Your group, in addition to searching the Internet, will look at part of the Association of the British Pharmaceutical Industry's publication *an A to Z of British Medicines Research*, given below and in Figure 1, and at a table of deaths from various diseases since 1935 (Table 1).

Here are some of the questions you might like to consider in your research and presentation.

- Is there a link between trends in deaths from disease and the discovery of medicines?
- What other causes of longevity are there as well as improvement of medicines?
- What are the main killers today? What will happen when they are tamed?
- Is death rate a good measure of the nation's health? What other measures are there?

Extract from *an A to Z of British Medicines Research*

The past fifty years of British medicines research

The past 50 years have seen a revolution in our understanding of disease and its treatment (Figure 1). It has been a half century in which:

- organ transplantation has become accepted as commonplace
- the structure of DNA was elucidated, opening the way for the sciences of genetic engineering and genomics
- interferon, the first of a family of naturally occurring molecules called cytokines, was isolated and named
- monoclonal antibodies were discovered, opening the way for the specific targeting of medicines
- smallpox, a centuries-old scourge of mankind, was eradicated from the planet

- techniques for *in vitro* fertilisation were developed, bringing family joy to many childless couples
- AIDS emerged and with it the discovery of a family of human viral pathogens called retroviruses, of which HIV is one, leading to entirely new medicines to contain the virus
- advanced scanning techniques were developed which have transformed the diagnosis and understanding of many human diseases.

Built on these and many other developments, there has also been a revolution in the number, specificity and safety of human medicines. It is here as much as anywhere that Britain has been in the front line: for the whole of the last half century, medical and medicines research in Britain has been the envy of the world for its innovative skills and high ethical standards. Even today, despite increasing pressure on funding and demands for greater safety in medical products, we still enjoy this reputation. British hospitals are often a first choice for assessing the value of new medicines. Many European, Japanese and American owned pharmaceutical companies choose to fund major research groups here. It is no accident that today 7 of the top 25 medicines in the world, and 6 of the top 12 medicines used to treat bacterial and viral infections, are the products of British pharmaceutical research.

But the industry can also be proud of the contribution it makes to the British economy. UK earnings from the export of medicines exceeded imports by £2.3 billion in 1997. On top of that, the industry employs the skills of more than 60 000 people, including 20 000 highly-trained scientists and doctors.

Disease	1935	1945	1955	1965	1975	1985	1995
Scarlet fever	499	82	21	1	–	–	–
Whooping cough	1473	689	88	21	12	4	2
Diphtheria	3408	694	13	–	1	–	1
Measles	1264	728	176	115	16	11	1
Typhoid	170	44	15	8	1	–	–
Tuberculosis (respiratory)	23 840	19 668	5837	2008	722	408	355
Syphilis	3521	2378	1385	857	110	40	9
Heart disease (circulatory system)	103 613	127 969	138 313	151 718	299 669	287 054	241 871
Cancer	62 602	73 753	91 340	106 474	123 769	141 618	140 791
Total deaths	477 401	481 274	518 864	549 379	582 841	590 734	565 902
Population (million)	40.65	42.63	44.44	47.67	49.47	49.99	51.52

Table 1 Deaths from various diseases in England and Wales, 1935–1995 (The Stationery Office Annual Abstract of Statistics)

A glossary of some of the diseases in the table

Scarlet fever Infectious disease. High fever, sore throat. Caused by streptococcal bacterial infection.

Whooping cough Infectious disease of mucous membrane of air passages. Frequent attacks of convulsive coughing caused by bacteria. Vaccination possible.

Diphtheria Infectious disease causing growth of membrane, often on tonsils, making swallowing difficult. The bacterium produces a toxin. Vaccination began in 1940.

Measles Viral infection. Causes fever and rash. Vaccine available.

Typhoid A fever with ulceration of skin and bowels. Bacteria carried in sewage which is main cause of contagion.

Tuberculosis Disease of lungs and other organs caused by bacteria. Improved hygiene, vaccination and chest X-rays have helped to minimise its effects.

Syphilis A sexually transmitted (or inherited) disease. Slow to manifest itself. Caused by a spirochaete. Results in death unless checked.

1948 • Pernicious anaemia shown to be caused by **Vitamin B12 deficiency**
• Antibiotics **chloramphenicol** and **chlortetracycline** (the first tetracycline) discovered
1949 • **Cortisone** shown to be active in rheumatoid arthritis
1950
1951
1952
1953 • ***DNA double helix*** *discovered by Watson and Crick*
1954 • *First successful* ***kidney transplantation*** *in US*
1955 • *First* ***oral treatment*** *for diabetes introduced (Germany)*
1956
1957 • ***Interferon*** *first isolated and named by Isaacs and Lindenman at NIMR, London*
• **Imipramine** shown to be effective in depression
• **Halothane** (ICI/Zeneca) anaesthetic gas introduced
1958
1959 • First **semi-synthetic penicillin** marketed
1960 • **Methicillin** launched – active against many resistant bacteria
• **Metronidazole** (Rhône-Poulenc) for parasitic and anaerobic bacterial infections
1961 • **Allopurinol** (Wellcome) developed for gout and arthritis
1962 • 1961–3 first **benzodiazepines** (Roche) for depression
• First oral contraceptive launched – **Anovlar** (Schering Health Care)
• **Azathioprine** (Wellcome) patented for immuno-suppression
1963 • **Ampicillin** (Beecham) major antibiotic discovered
1964 • **Ibuprofen/Flurbiprofen** (Boots) for arthritis and inflammation
1965 • **Propranolol** (ICI/Zeneca) a beta-blocker for heart disease
1966
1967 • **Becotide** (Allen & Hanbury's) for asthma
• *First* ***heart transplant*** *by Christiaan Barnard in South Africa*
1968 • **Sodium cromoglycate** (Fisons) breakthrough in asthma
1969 • **Salbutamol** (Glaxo) introduced for asthma
1970 • **Levodopa (L-dopa)** a major advance in Parkinson's
1971 • *Mechanism of action of* ***aspirin*** *discovered by Sir John Vane*
1972
1973 • **Tamoxifen** (ICI/Zeneca) introduced for hormone-dependent tumours
1974
1975 • ***Monoclonal antibodies*** *discovered by Kohler and Milstein (UK)*
• **Clozapine** (Novartis) first atypical neuroleptic for schizophrenia enters clinical trial
• **Clotrimazole** (Bayer) a major advance in treating fungal infections
• **Nifedipine** (Bayer) for angina and hypertension
1976 • **Atenolol** (ICI/Zeneca) a beta-blocker introduced for various heart conditions
• **Cyclosporin** (Novartis) a major advance in transplantation
• **Cimetidine** (SmithKline Beecham) launched for peptic ulcers

1977
1978 • *Birth of Louise Brown after Steptoe and Edwards develop* ***in vitro Fertilisation***
• **Ranitidine** (Glaxo) anti-ulcer treatment discovered
1979 • ***Smallpox*** *eradicated from the world*
• ***Interferon gene*** *first cloned*
1980
1981 • **Captopril** (Bristol-Myers Squibb) first ACE inhibitor for high blood pressure
1982 • **Fluconazole** (Pfizer) – key advance in treating fungal infections
1983 • *Sir John Vane awarded Nobel Prize for work on* ***aspirin*** *and* ***prostaglandins***
• *Isolation of* ***HIV*** *as the cause of AIDS*
• **Sumatriptan** (Glaxo) – major advance in migraine
1984 • **Cholestyramine** – trial shows lowering of cholestrol and coronary heart disease
• Antibiotic **Augmentin** (Beecham) launched
1985 • **Acyclovir** (Wellcome) treatment for herpes launched
1986 • ACE inhibitor **enalapril** (MSD) launched for high blood pressure
• **Orthoclone** (Ortho) for transplantation – first licensed human monoclonal antibody
1987 • **Zidovudine** (Wellcome) – first AIDS treatment launched
1988 • **Lisinopril** (ICI/Zeneca) ACE inhibitor for hypertension and heart failure
• *Nobel Prize awarded to* ***Sir James Black*** *for medicines discovery*
• **Diclofenac** (Novartis), an anti-inflammatory agent, launched
• **Erythropoietin** (Janssen-Cilag), natural red blood cell stimulator, launched in the UK
1989 • **Omeprazole** (Astra) launched for gastric ulcers
• **Simvastatin** (MSD) launched for lowering blood lipids
• **Fluoxetine** (Eli Lilly) launched for depression
1990 • ***COX-2****, a major new target for anti-inflammatory drugs, discovered by scientists at Searle*
• *First* ***gene therapy*** *experiment in a person with adenosine deaminase deficiency*
1991 • **Filgrastim** (Amgen) white blood-cell stimulant, G-CSF launched in UK
1992 • **Etidronate** (Procter & Gamble). First bis-phosphonate in UK for osteoporosis
1993
1994
1995 • **Lamotrigine** (Wellcome) – major advance launched as monotherapy in epilepsy treatment
• **Interferon beta-1b** (Schering Health Care) – first treatment for multiple sclerosis
1996 • **Olanzapine** (Eli Lilly) introduced for schizophrenia
• **Ropinirole** (SmithKline Beecham) launched for Parkinson's
• **Saquinavir** (Roche) launched – first protease inhibitor for AIDS in UK
1997 • First medicines for Alzheimer's disease available – **Donepezil** (Pfizer) and **Tacrine** (Parke-Davis)
• **Latanoprost** (Pharmacia & Upjohn) first prostaglandin analogue for glaucoma
• **Reboxetine** (Pharmacia & Upjohn) first noradrenaline reuptake inhibitor for depression

Figure 1 Time line of some major discoveries in medicines research 1948–1997

3: The British pharmaceutical industry

Search the Internet and look at the data provided (which come from The Association of the British Pharmaceutical Industry).

Here are some of the questions you may wish to address in your research and presentation.

- How important is the pharmaceutical industry in national terms to the economy?
- How has the industry grown over the years?
- Into which categories can the products of the industry be usefully divided?
- How important is the British pharmaceutical industry internationally?

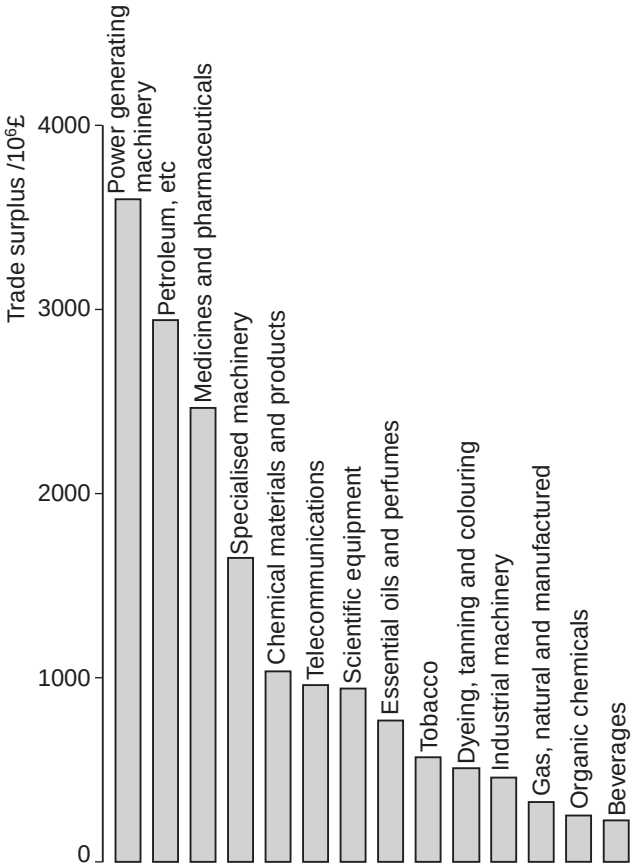
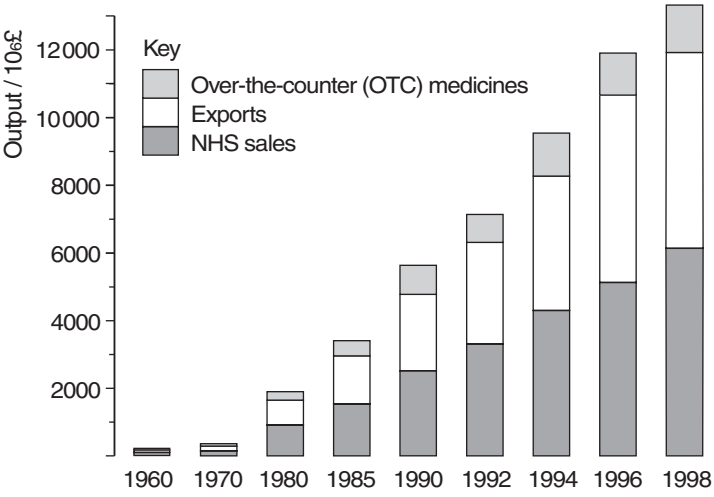


Figure 1 UK visible trade surpluses in 1998



Source: *Pharma, Facts and Figures*, Association of the British Pharmaceutical Industry, 2000

Figure 2 British pharmaceutical industry output by market sectors

	Exports /10^6£	Imports /10^6£	Balance /10^6£	Exports per employee/£	All UK exports per employee /£
1981	852	298	554	12 206	6345
1982	978	375	603	14 257	7088
1983	1074	470	604	15 817	7978
1984	1222	542	680	18 077	9420
1985	1426	590	835	21 315	10 520
1986	1533	679	853	23 991	11 205
1987	1621	786	835	24 339	12 712
1988	1735	876	859	25 628	13 675
1989	2016	1062	955	28 315	15 816
1990	2258	1158	1100	31 759	17 873
1991	2556	1371	1184	35 104	20 019
1992	2993	1663	1330	40 553	21 744
1993	3710	2019	1691	53 927	25 113
1994	4005	2304	1701	57 705	28 582
1995	4939	2812	2126	79 784	31 925
1996	5386	3107	2279	91 597	34 386
1997	5455	3192	2262	90 912*	35 496
1998	5860	3418	2442	97 667*	

Table 2 British pharmaceutical trade figures

*Subject to revision

Source: *Pharma, Facts and Figures*, Association of the British Pharmaceutical Industry, 2000

	Exports /10^6£	Imports /10^6£	Trade balance /10^6£
Germany	7741	4179	3562
Switzerland	4904	2115	2790
UK	5860	3418	2442
Ireland	2620	486	2134
France	5193	3507	1685
Sweden	2142	739	1403
Belgium	3056	2380	676
Denmark	620	471	150
Netherlands	1967	2043	–76
Austria	809	1058	–249
Italy	2344	2596	–252
Finland	138	394	–255
Portugal	87	441	–358
Greece	70	600	–530
Australia	393	988	–596
Spain	743	1572	–828
Canada	675	1525	–850
US	4817	5687	–870
Japan	686	1948	–1262

Table 3 World pharmaceutical trade figures, 1998

Source: *Pharma, Facts and Figures*, Association of the British Pharmaceutical Industry, 2000

WM2

Extraction of salicylic acid

In this activity you can extract some salicylic acid, a pharmacologically active compound from a natural source, oil of wintergreen, which is obtained in turn from the shrub* Gaultheriae procumbus. *You then learn the technique of thin-layer chromatography and use it to compare the extract with a pure sample of salicylic acid.

Requirements

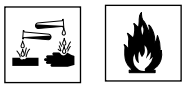
- oil of wintergreen (2 cm^3)
- apparatus for heating under reflux (see Figure 1)
- sodium hydroxide solution, 2 mol dm^{-3} (25 cm^3)
- measuring cylinder (25 cm^3)
- anti-bumping granules
- small Bunsen burner or electric heating mantle
- 100 cm^3 beakers (2)
- ice (if available)
- concentrated hydrochloric acid (a few cm^3)
- Universal Indicator paper
- glass rod
- Buchner funnel and apparatus for vacuum filtration
- watch glass
- ethanol (a few cm^3)
- t.l.c. plates (silica-coated)
- small beaker to hold t.l.c. plate
- cover for the beaker
- solution of salicylic acid in ethanol (1 cm^3)
- solvent for chromatography – cyclohexane, ethyl ethanoate, ethanoic acid (200:100:1)
- dropping tubes or melting-point tubes (2)
- u.v. light source
- iodine crystals
- aluminium foil or clingfilm

CARE Ultraviolet radiation is harmful to the eyes. Do not look directly at the lamp. Follow the recommended precautions concerning eye protection.

CARE Eye protection must be worn.

cyclohexane

glacial ethanoic acid



ethanol

ethyl ethanoate

concentrated hydrochloric acid

2-hydroxybenzoic acid (salicylic acid)

iodine

methyl 2-hydroxybenzoate, methyl salicylate (oil of wintergreen)

sodium hydroxide solution

Introduction

The ester methyl salicylate found in nature can be converted into salicylic acid. It is obtained as oil of wintergreen which used to be made by dry distillation of the leaves of the evergreen shrub *Gaultheriae procumbus* prevalent in the US. You may be familiar with the smell of the ester for it is present in many medicinal preparations (for example 'Deep Heat' and other similar ointments used to relieve muscle pain).

In this experiment you will obtain salicylic acid from the methyl ester by hydrolysis, using dilute sodium hydroxide solution.

What you do

1 Put about 2 cm^3 of oil of wintergreen (**CARE** Harmful) into a 50 cm^3 pear-shaped flask and add 25 cm^3 of 2 mol dm^{-3} sodium hydroxide solution (**CARE** Corrosive) together with a few anti-bumping granules.

2 Attach a water condenser to the flask in a vertical position (see Figure 1) and gently heat the mixture under reflux for 30 minutes. Make sure the condenser water supply is on. You can heat the flask with a small Bunsen flame below a wire gauze or use an electric heating mantle. When the mixture is boiling, condensed droplets should be falling back into the flask at a rate of about 1 drop per second.

3 Allow the mixture to cool and pour it into a 100 cm^3 beaker surrounded by cold water (and ice, if available). Using a dropper, add concentrated hydrochloric acid drop by drop (**CARE** Corrosive) until the mixture is acidic. Test the mixture, as you add the acid, with Universal Indicator paper, using a glass rod and small drops of the mixture.

4 Using a Buchner funnel, filter the product using vacuum filtration. Wash the solid with a little cold water and transfer it to a watch glass.

5 Take a few crystals of the product and dissolve them in a minimum of ethanol.

6 Take a pre-dried thin-layer chromatography plate which will fit into a small beaker (see Figure 2). About 1 cm from the bottom of the plate draw a fine pencil baseline. On the line place a small spot of the extract from stage **5**. On the baseline also put a small spot of a solution of salicylic acid in ethanol. The spots are best made using a very fine dropping pipette or a drawn-out melting-point tube. Apply a small quantity of the solution at a time; let it dry, and then add more. Try not to let the diameter of the drops exceed 5 mm.

7 Place some solvent for the chromatograpy in the beaker to a depth of about 5 mm. (**CARE** Highly flammable. Avoid breathing the vapour.)

8 Place the chromatography plate in the beaker, making sure the solvent is below the pencil line on the plate.

9 Cover the beaker, for example with aluminium foil or a watch glass. Leave the solvent to rise up. This will take about 15–25 minutes.

10 When the solvent has nearly reached the top of the plate, take the chromatogram out of the beaker. (**CARE** Avoid breathing the solvent vapour.) Place the plate in a fume cupboard and allow the solvent to evaporate.

11 You can locate the positions of the substances on the plate by examining it under u.v. light. (**CARE** Do not look directly at the light source.) View the plate by reflected light.

12 Alternatively, place the sheet in another beaker with a few crystals of iodine (**CARE** Harmful. Avoid skin contact. Use in a fume cupboard.) Cover the beaker with aluminium foil or clingfilm. The spots which were probably just visible before should show up more clearly now. After the experiment, dispose of the solvent as directed by your teacher.

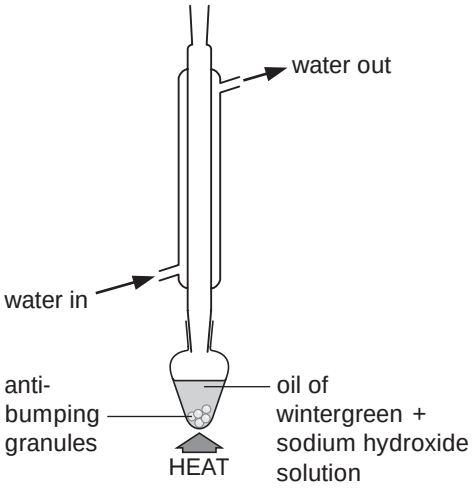


Figure 1 Apparatus for heating under reflux

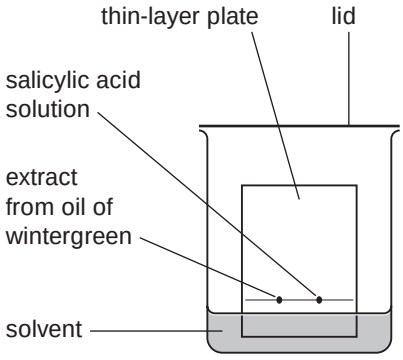


Figure 2 Apparatus for thin-layer chromatography

QUESTIONS

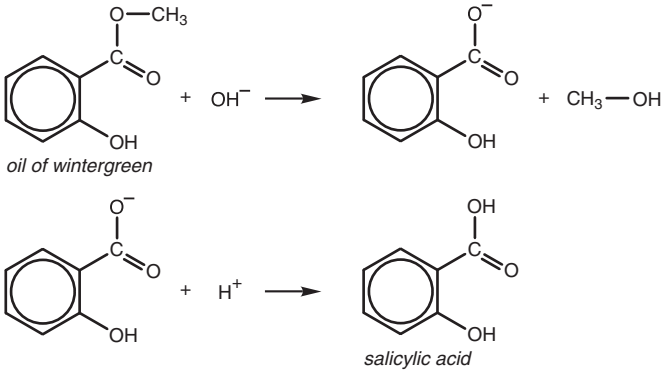
a Explain what is meant by *heating under reflux*. Why is this often necessary when heating organic liquids?

b Why is it necessary to heat the flask for such a long time?

c What do the results from the thin-layer chromatography separation tell you about the composition of the extract from oil of wintergreen?

d The equations for the reactions occurring in the experiment are shown on the right. How could you have obtained the methanol formed during the experiment if you had wished to use it?

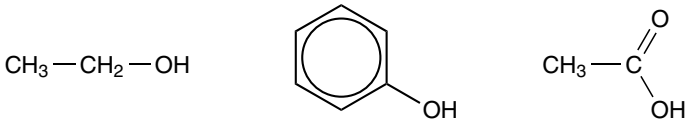
e Suggest why the mixture formed by the hydrolysis of the ester was kept as cool as possible.



WM3

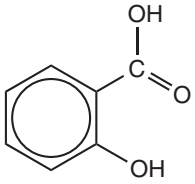
Investigating the chemistry of the –OH group in various environments

The hydroxyl (–OH) group occurs in three types of organic compound: alcohols, phenols and carboxylic acids. Examples are:



ethanol *phenol* *ethanoic acid*

The object of this activity is to investigate the behaviour of the –OH group in these three compounds and to compare this with the behaviour of 2-hydroxybenzoic acid (salicylic acid).



2-hydroxybenzoic acid (salicylic acid)

Requirements

- small quantities of:
  - ethanol
  - phenol (saturated solution in water)
  - ethanoic acid (2 mol dm^{-3} solution)
  - glacial ethanoic acid (for test **5**)
  - 2-hydroxybenzoic acid (salicylic acid)
- protective gloves
- Universal Indicator solution
- iron(III) chloride solid
- methanol (5 cm^3)
- concentrated sulphuric acid (access to bottle)
- sulphuric acid, 2 mol dm^{-3} (5 cm^3)
- sodium carbonate solution, approximately 0.5 mol dm^{-3} (200 cm^3)
- test-tubes
- 100 cm^3 beakers
- source of hot water

glacial ethanoic acid

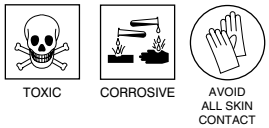
ethanol

2-hydroxybenzoic acid (salicylic acid)

iron (III) chloride

methanol

phenol



sulphuric acid

CARE Phenol can cause sores and blistering if spilt on the skin. Glycerol, propane-1,2,3-triol, can be applied to counteract phenol burns.

CARE 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 vapour.

CARE Eye protection and gloves must be worn.

Comparing ethanol, phenol, ethanoic acid and 2-hydroxybenzoic acid

Look quickly through the tests you will be doing, and draw up a table to present your results.

For each test use 1 cm depth of the sample solution or a small spatula measure of solid.

What you do

1 To each of the four substances in turn add a few drops of Universal Indicator solution, and record the pH value.

2 To each of the substances in turn add an equal volume of aqueous sodium carbonate and warm. Test for any gas evolved.

3 Dissolve a small spatula measure of solid iron(III) chloride (**CARE** Irritant; stains skin and clothing) in about half a test-tube of water. Divide the solution equally among four test-tubes and add a small quantity of each substance in turn to the tubes. Record any colour changes.

4 **Cautiously** smell samples of each of the four substances in turn. Make a note of their smells.

5 Put 1 cm^3 of each substance in turn into a test-tube. In the case of ethanoic acid, use the concentrated ('glacial') acid rather than an aqueous solution. (**CARE** Concentrated ethanoic acid is corrosive and flammable.) Then to each add an equal volume of methanol and a few drops of concentrated sulphuric acid (**CARE** Corrosive). Warm each tube and its contents gently for a few minutes in hot water in a beaker. Pour the hot solutions into beakers of dilute sodium carbonate solution. This neutralises any acid which remains and so removes its smell. **Cautiously** smell the contents of the beakers. Note any changes of smell.

What do you do if the organic material catches fire?

Do not panic!

Place the test-tube in the rack and place a wet cloth over the top.

Do not run around with the test-tube on fire.

Do not use a fire extinguisher for a small fire in a test-tube.

QUESTIONS

a Look at the results of the tests for 2-hydroxybenzoic acid. In what way does it show similarities to those for the other compounds?

b What conclusion can you draw about the environments of the –OH groups in 2-hydroxybenzoic acid?

WM4

Interpretation of the mass spectrum of salicylic acid

In this activity you will practise some of the ideas you are learning about mass spectrometry, and see how chemists can identify a substance from its mass spectrum.

***Before starting the activity you should be familiar with the technique of mass spectrometry. If necessary, read about this in* Chemical Ideas 6.5.**

This activity guides you through a sequence of steps which a chemist could take when using mass spectra data to confirm the structure of a substance extracted from willow bark and given the name salicylic acid. You can record the evidence as you acquire it on the **Information Sheet** (*Mass spectrum data*). Remember research chemists, when publishing their findings, must supply as much evidence as possible to confirm the structure they propose for a compound even if, when more limited evidence is available, they already feel confident about the structure.

Finding possible formulae

1 Look first at Figure 1, the mass spectrum of salicylic acid. Measure the relative abundance of the six marked peaks. Record the mass and abundance of each peak in the appropriate box towards the bottom of the **Information Sheet**.

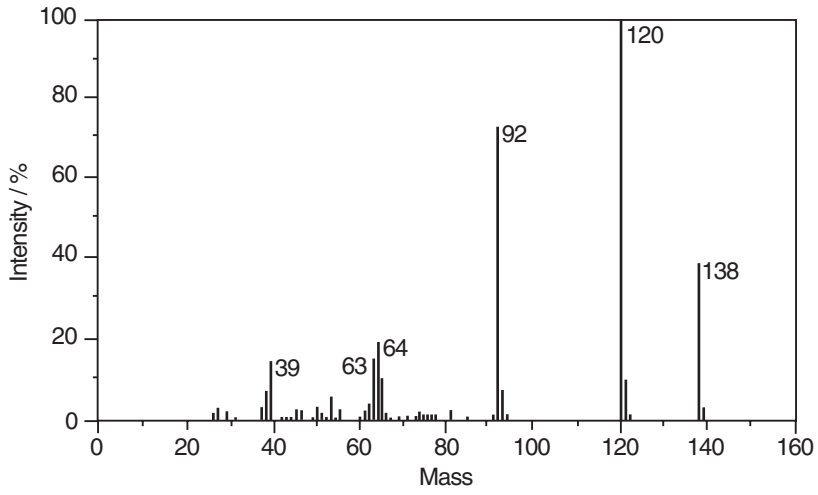


Figure 1 The mass spectrum of salicylic acid

2 Decide which of these peaks gives the molecular mass of the compound.

A computer database can list the possible molecular formulae that will fit this value. There can of course be a very large number. One limited database gives 38 compounds for this molecular mass. Add this number to the **Information Sheet**.

Using isotope peaks to establish the formula

The number of possible compounds can be reduced by using the high-resolution mass spectrum facility. For the willow bark extract this gives an accurate molecular mass of 138.0317. In the same database there are only two compounds with this value: they are $C_2H_7ON_4Cl$ and $C_7H_6O_3$. Add these possible molecular formulae to the **Information Sheet**.

Naturally occurring carbon consists of a mixture of isotopes. Most carbon is ^{12}C, but ^{13}C is present as 1.1% of the sample. If the active chemical in the extract contains one carbon atom in its molecule, the molecular ion peak at a mass M should be accompanied by another peak at M+1 with approximately 1.1% the intensity of the molecular ion peak. Two carbons will give rise to an M+1 peak of approximately 2.2% relative intensity, and so on.

This means that for one carbon atom, the ratio of the intensities of M : M+1 peaks will be 98.9 : 1.1; for two carbon atoms the ratio will be 97.8 : 2.2, and so on.

3 Figure 2 gives a more accurate mass spectrum for salicylic acid. This spectrum shows any isotope peaks which exist. The intensities of the molecular ion peaks have been accurately measured and are given on the **Information Sheet**.

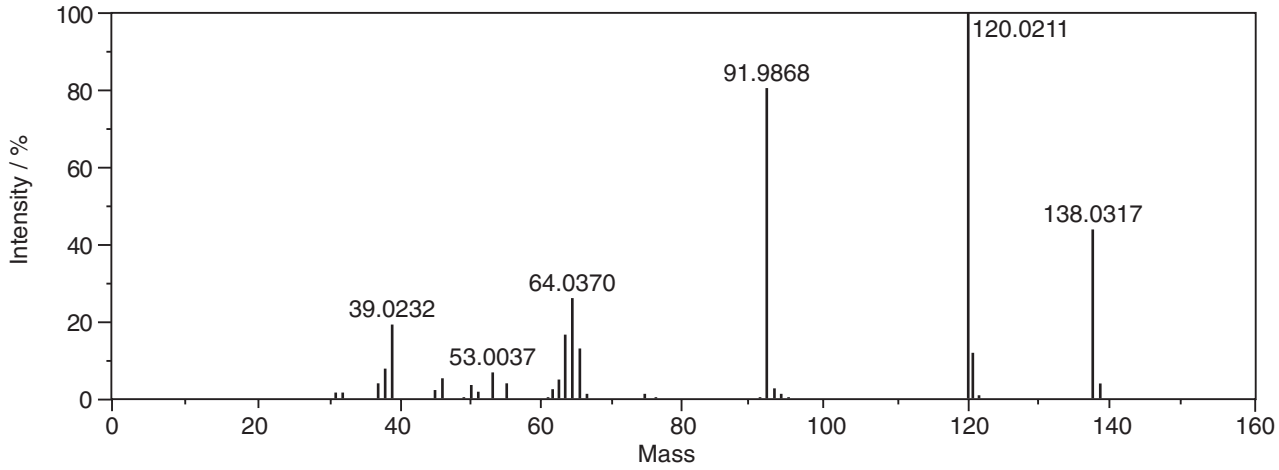


Figure 2 A more accurate version of the mass spectrum of salycylic acid

Using a database to establish which isomer it is

A web site, which supplies mass spectra of compounds, indicates that there are three isomers with the molecular formula $C_7H_6O_3$. The mass spectra of these compounds provides the following information.

2-hydroxybenzoic acid						
Peak	120	92	138	64	39	63
Intensity	100	73	39	19	14	14
3-hydroxybenzoic acid						
Peak	138	121	93	65	39	91
Intensity	100	75	23	16	12	12
4-hydroxybenzoic acid						
Peak	121	138	65	93	39	63
Intensity	100	83	24	22	18	10

Table 1 Mass spectra of the three hydroxybenzoic acids

4 Which of these matches the spectrum of salicylic acid? Write the chemical name and structure of salicylic acid on the **Information Sheet**.

Confirming the structure using the fragmentation pattern

Mass spectrometrists can find out a lot about the structure of a molecule by looking at the fragmentation pattern in the mass spectrum. This provides an additional way of distinguishing 2-hydroxybenzoic acid from its two isomers, 3- and 4-hydroxybenzoic acid. It may help with this activity to build models of the three molecules.

5 Using Table 1, write down the peaks in the mass spectrum of 2-hydroxybenzoic acid that are not shared by 3- and 4-hydroxybenzoic acid.

6 Which well-known molecule with $M_r = 18$ might be lost in the conversion:

138 (the whole molecule) → 120

in 2-hydroxybenzoic acid?

7 What are the two most likely ways in which the molecule in **6** can arise from 2-hydroxybenzoic acid? Show this by ringing the relevant atoms on drawings of the structure of the molecular ion of 2-hydroxybenzoic acid (Figure 3).

8 3- and 4-hydroxybenzoic acid do not have the same fragmentation pattern because they cannot form an ion of mass = 120. Explain why this ion cannot form.

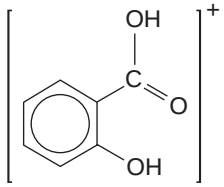


Figure 3 The molecular ion of 2-hydroxybenzoic acid

Information Sheet: Mass spectrum data

Approximate molecular mass
(found by fast, low-resolution scan)

Number of possible molecular formulae

Accurate molecular mass
(measured by slower, high-resolution scan)

Possible molecular formulae

Isotope peaks

A group of peaks starting at the parent ion peak, due to isotopes of carbon. These peaks may be small on the spectrum, but are given here scaled up so that the largest peak in this group has abundance 100.

Molecular ion peak = 100% Indicated number of carbon atoms:
M + 1 peak = 8.2%

Six largest peaks in the spectrum

Mass						
Relative abundance						

Identity of this sample

WM5.1

A preparation of aspirin

This activity is an example of an organic preparation. You will be able to purify and test your product.

Requirements

- 100 cm^3 conical flask
- 10 cm^3 measuring cylinders (2)
- 100 cm^3 beaker
- glass rod
- apparatus for vacuum filtration
- Hirsch funnel
- 2-hydroxybenzoic acid (salicylic acid) (2 g)
- ethanoic anhydride (4 cm^3)
- concentrated sulphuric acid (5 drops)
- ethanoic acid (glacial) (4 cm^3)
- water bath containing crushed ice
- source of hot water
- test-tubes (4)
- aspirin (1 crystal)
- neutral iron(III) chloride solution (1 cm^3)

ethanoic acid

CORROSIVE

ethanoic anhydride

CORROSIVE

2-hydroxybenzoic acid (salicylic acid)

IRRITANT

iron (III) chloride

IRRITANT

concentrated sulphuric acid

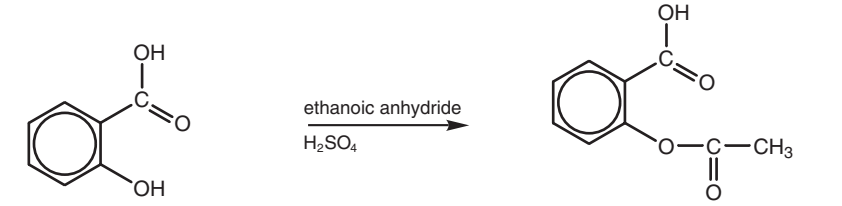
CORROSIVE

CARE Eye protection must be worn.

WEAR EYE PROTECTION

Introduction

Aspirin (acetylsalicylic acid or 2-ethanoylhydroxybenzoic acid) can be made by a variety of methods but they all start from 2-hydroxybenzoic acid (salicylic acid).



2-hydroxybenzoic acid *2-ethanoylhydroxybenzoic acid*

What you do

1. Shake 2 g of 2-hydroxybenzoic acid (salicylic acid) (**CARE** Irritant) with 4 cm^3 of ethanoic anhydride (**CARE** Corrosive) in a 100 cm^3 conical flask.
2. Add five drops of concentrated sulphuric acid (**CARE** Corrosive) and continue agitating the flask for about 10 minutes. Crystals of aspirin will appear and soon the whole will form a crystalline mush.
3. Dilute by stirring in 4 cm^3 of cold glacial ethanoic acid (**CARE** Corrosive) and cool by placing in a water bath containing crushed ice.
4. Filter off the crystals using a Hirsch funnel (a small funnel for vacuum filtration), washing once with ice cold water. Reserve a few crystals for testing later.
5. Place the crude aspirin in a 100 cm^3 beaker. Add hot, but not boiling, water until it dissolves. Cool and filter off the crystals. This process is known as **recrystallisation** and is a way of purifying a solid product.
6. Take four test-tubes and add 2 cm^3 of distilled water to each.
   To one tube add one crystal of the product before recrystallisation and shake.
   To another add one crystal of the recrystallised product and shake.
   To another add one crystal of 2-hydroxybenzoic acid and shake.
   To the last add one crystal of known pure aspirin and shake.
   To each tube in turn add 2 drops of neutral iron(III) chloride solution (**CARE** Irritant) and shake.

QUESTIONS

a On the basis of your observations in part **6**, was your product pure aspirin?

b A student obtained 1.7 g of dry product. Calculate the percentage yield.

c Explain why recrystallisation should produce a purer product.

d There are several ways of testing the purity of the product:

i neutral iron(III) chloride solution

ii thin-layer chromatography

iii melting point.

Explain with the aid of a diagram how you would use thin-layer chromatography to test the purity of a sample of aspirin.

WM5.2

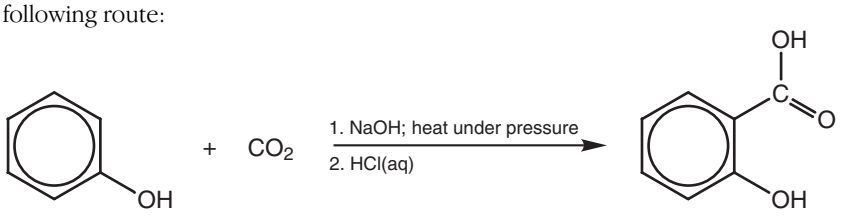
Using spectroscopy

In this activity you will analyse the infrared and mass spectra of some organic molecules used in the synthesis of the medicine, aspirin.

For this activity you will need to refer to the characteristic i.r. absorption frequencies given in the **Data Sheets**.

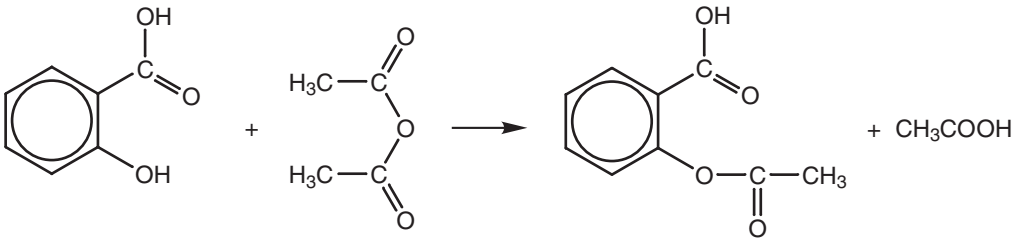
Aspirin, 2-ethanoylhydroxybenzoic acid, is manufactured commercially from phenol by the following route:

Step 1



phenol (A) — *2-hydroxybenzoic acid* (B)

Step 2



ethanoic anhydride — *aspirin* (C)

QUESTIONS

a The i.r. and mass spectra of compounds A, B and C are given in Figures 1–3 on the next sheet.
Identify, with as much explanation as possible, which set of spectra (Figure 1, 2 or 3) corresponds to each of the compounds A, B and C.

b Use the data of % composition by mass, given in Table 1, to confirm your answer to part **a**.

Compound	%C	%H	%O
Figure 1	60.9	4.3	34.8
Figure 2	60.0	4.4	35.6
Figure 3	76.6	6.4	17.0

Table 1 Composition by mass

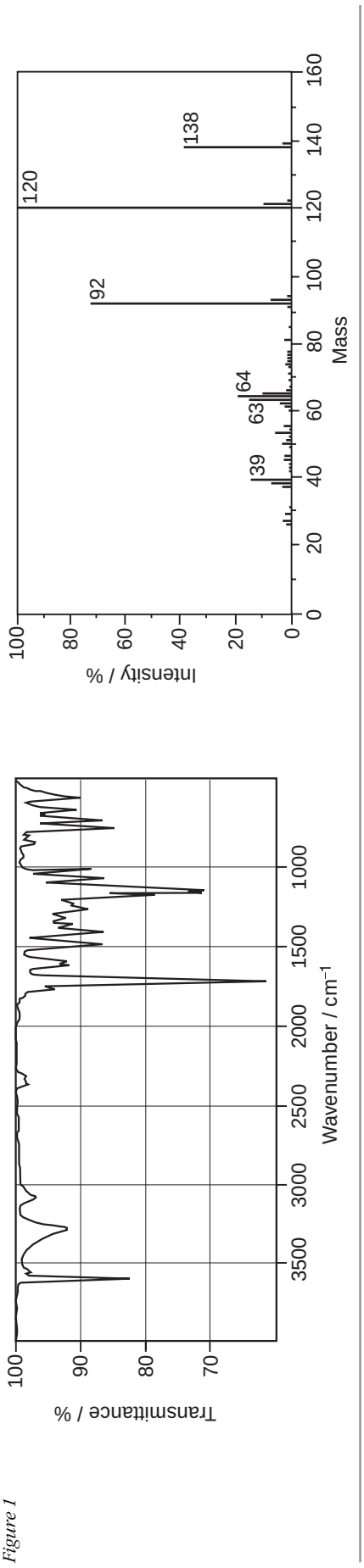


Figure 1

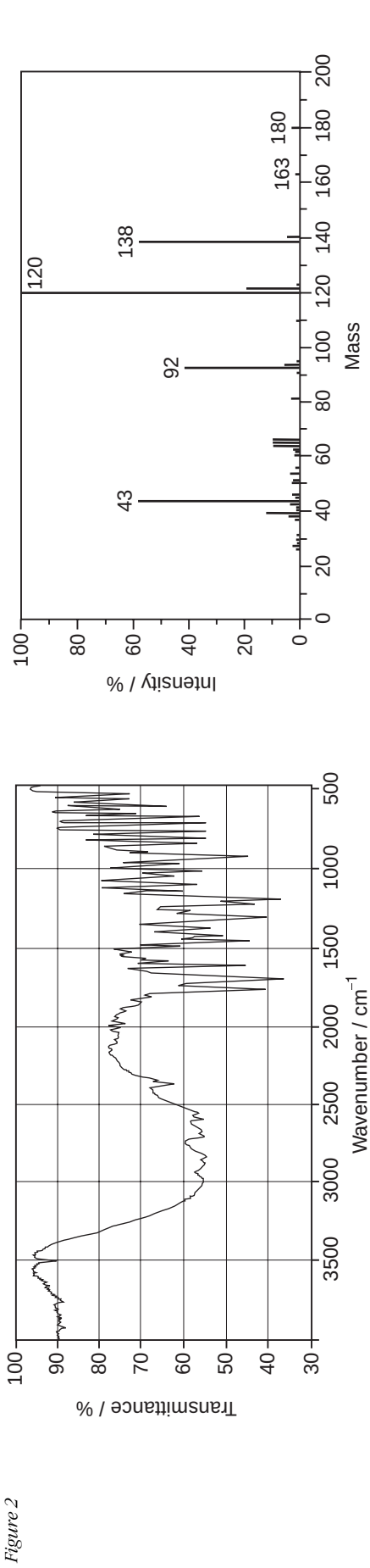


Figure 2

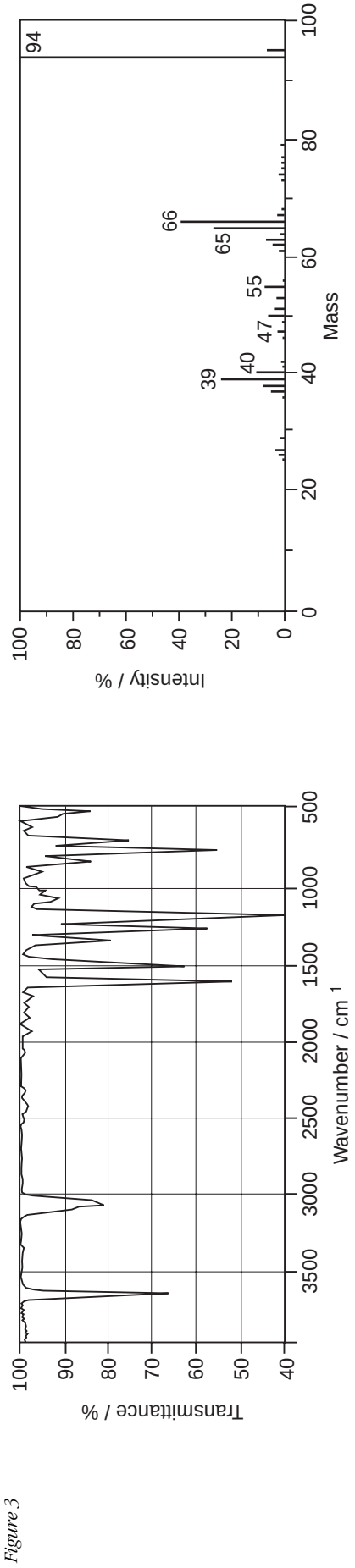


Figure 3

WM6

An aspirin assay

In this activity you will follow the method used by hospital analysts to check the purity of aspirin samples before they are considered fit to be used on the wards.

Requirements

- aspirin tablets (300 mg)
- mortar and pestle
- specimen tubes (3)
- access to a balance
- 100 cm^3 conical flask
- 95% ethanol (30 cm^3)
- 10 cm^3 measuring cylinder
- sodium hydroxide solution, 0.1 mol dm^{-3} (60 cm^3)
- burette
- Phenolphthalein indicator

ethanol

HIGHLY FLAMMABLE

CARE Eye protection must be worn.

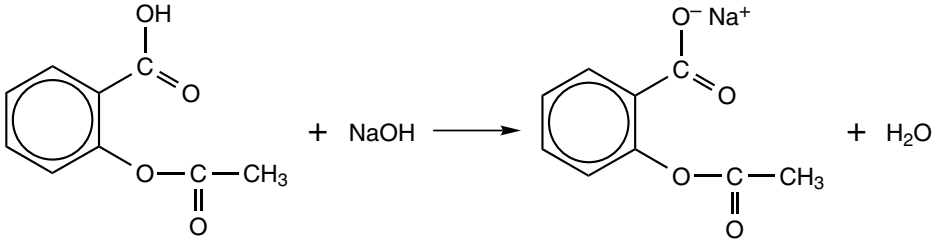
WEAR EYE PROTECTION

What you do

1. Grind up 1 aspirin tablet using a mortar and pestle.
2. Transfer as much of the powder as possible into a specimen tube. Weigh the tube to an accuracy of 1 mg, and record the mass.
3. Use a measuring cylinder to place 10 cm^3 of 95% ethanol into a 100 cm^3 conical flask. Add a few drops of Phenolphthalein indicator. Then add as much of the powdered aspirin as you can from the specimen tube.
4. Reweigh the specimen tube to the same accuracy as before and record the mass.
5. Swirl the conical flask carefully until all the aspirin powder has dissolved. Do not allow any of the solution to splash out of the flask.
6. Titrate the solution in the flask with 0.1 mol dm^{-3} sodium hydroxide solution from a burette (**CARE** Eye protection *must* be worn). Record the volume needed to produce the first tinge of pale pink colour in the indicator. This measures the end-point of the titration.
7. Repeat the procedure at least once more, starting with a fresh aspirin tablet.

Calculation

The equation for the reaction used in the assay is:



Notice that 1 mol of aspirin reacts with 1 mol of sodium hydroxide. (Actually, if you were to heat the reaction mixture, a further reaction would take place and the ester would be hydrolysed. But at room temperature this does not happen.)

1 mol of aspirin has mass of 180.2 g.

Concentration of sodium hydroxide solution = …… mol dm^{-3}

8 Calculate the purity of the aspirin tablet, using Table 1.

	Assay 1	Assay 2	Assay 3
Mass of specimen tube + aspirin powder/g			
Mass of specimen tube after pouring out aspirin powder/g			
Mass of aspirin used/g			
Volume of sodium hydroxide solution used/cm^3			
Amount of sodium hydroxide used/mol			
Amount of aspirin which reacted with sodium hydroxide/mol			
Mass of aspirin which reacted with sodium hydroxide/g			
Aspirin in powder used/%			

Table 1

Evaluating your results and procedures

a What is the percentage error in your measurement of the mass of aspirin used and in the volume of sodium hydroxide solution used?

b Identify any stages in your *procedure* which could have led to errors. Comment on the range of answers obtained for your three assays.

c Bearing in mind the sources of error you have discussed above, how many significant figures do you think you are justified in using for the percentage of aspirin in the powder?

9 Accurately weigh one aspirin tablet. Use your assay results to calculate the mass of aspirin contained in the tablet. Suggest why the mass of the tablet and the mass of aspirin may be different. Why do you think the tablets are described as '300 mg' tablets?

WM8

Which product should a pharmaceutical company develop?

In the exercise that follows, you are asked to take on the role of a manager in a pharmaceutical company helping to make decisions about which products your company should develop.

General information

It is a very long process from the initial discovery of a compound which has some pharmacological activity to the final marketing of a medicine. At any one time, several different compounds may be available for further development, but the process is so expensive that a company must select only a limited number of compounds for further investigation.

Policies are reviewed at regular intervals and the progress of work on any one compound will be scrutinised at several key stages of development.

In this exercise, you need to be organised into groups which represent different management groups in a company. Some of the groups will make an 'initial technological and economic appraisal' of two potential pharmaceuticals; the other groups will make a 'second technological and economic appraisal' of the same two compounds.

Initial technological and economic appraisal

This is the stage at which the compounds under review have been identified, synthetic routes have been established and some preliminary testing for activity and toxicity is complete. The research division of the company have put forward two compounds, AP1011 and H2202, to be considered for further development.

You must consider the evidence available and produce, for each of these compounds, a summary of the arguments for and against taking up the option of further development work. Since the company budget may only allow for work on one of these, you should also recommend which seems the more promising compound to develop.

Second technological and economic appraisal

This comes after further development has been carried out. For the purpose of the exercise, it is assumed that the company adopted both compounds at the earlier stage and has since completed clinical trials and further studies of the behaviour of the compound in the body. Once again, the available evidence must be examined to produce a summary of the points for and against proceeding with each of the compounds, and you must recommend which should be developed and marketed.

When the evaluations have been completed, groups which have made the initial appraisal should compare their conclusions with groups which made the second appraisal.

Initial technological and economic appraisal

Technical information on compound AP1011

This compound has antipyretic (fever-reducing) and analgesic (pain-relieving) properties and so may be suitable for conditions such as toothache, headache, neuralgia, sciatica, period pains and pains in ligaments, muscles and joints. It also reduces swelling and pain in arthritis and rheumatic fever. There is some evidence that it may inhibit blood-clotting.

Preparation and stability AP1011 may be synthesised simply in two stages, both with high yield, from readily available and cheap raw materials. It seems likely that scaling-up of this synthesis will present no major problems. Estimated cost of large-scale production is approximately 20p per 100 g. AP1011 has already been shown to be stable in dry conditions for over two years.

It must be administered by mouth and can be formulated into tablets or as powder for dispersal in water.

Action AP1011 is a drug precursor in that it is hydrolysed in the stomach and small intestine to form an active metabolite which is absorbed through the intestinal wall into the bloodstream.

Indications from preliminary trials No major side-effects have been found. There is no evidence of carcinogenic effects. The compound may produce stomach irritation and causes nausea, vomiting and/or stomach bleeding in a few cases.

Overdose can lead to a number of symptoms, including confusion and respiratory problems.

The LD_{50} is estimated to be 1750 mg/kg of body weight.*

* The toxicity of a compound is tested by finding the dose which will kill 50% of a trial group of animals (usually rats). The dose is measured in terms of the number of milligrams of compound per kilogram of body weight of the animal.

Initial technological and economic appraisal

Technical information on compound H2202

This compound has mild sedative and hypnotic (sleep-inducing) effects and could thus fill the gap between mild pain-relieving sedatives like paracetamol and the benzodiazepines like Valium and Mogadon, which can be addictive with prolonged use.

Preparation and stability Synthesis is by a two-stage process from benzene-1,2-dicarboxylic acid and glutamic acid. Both are currently manufactured as intermediates in the production of other compounds. Scaling-up is likely to be moderately complex and the predicted cost is about £7.00 per 100 g.

The compound should be taken by mouth and can be made up into tablets. It is stable in storage.

Action H2202 is hydrolysed by the body reforming benzene-1,2-dicarboxylic acid, glutamic acid and ammonia.

Indications from preliminary trials Side-effects are almost nil. H2202 shows no toxic effects (even on fairly extreme overdose), and does not affect the liver or kidneys.

Prolonged high dosage can lead to slight disturbance of the nervous system, but this is reversed on reduction of the dose.

The LD_{50} is estimated to be 5000 mg/kg of body weight.*

* The toxicity of a compound is tested by finding the dose which will kill 50% of a trial group of animals (usually rats). The dose is measured in terms of the number of milligrams of compound per kilogram of body weight of the animal.

Second technological and economic appraisal

Technical information on compound AP1011

AP1011 has both antipyretic (fever-reducing) and analgesic (pain-relieving) properties. It is recommended for conditions involving 'mild' pain, including toothache, headache, neuralgia, sciatica, period pains and pains in ligaments, muscles and joints. For these purposes the dose rate is 600–900 mg repeated every 3–4 hours to a maximum of 4 doses in any 24 hours.

It has been shown to be remarkably effective in reducing swelling and pain in arthritis and rheumatic fever. For these purposes higher doses of up to 4 g per day (with corresponding increase in side-effects) may be needed.

It also has an effect of inhibiting blood-clotting and so may be used in low dose (100–200 mg per day) in inhibiting thrombosis.

Manufacture, storage and distribution AP1011 can be prepared on the semi-technical scale (kilogram quantities) in high purity and good yield. The predicted manufacturing cost is 35p per 100 g. There are no problems with large-scale supply of feedstock chemicals of adequate purity.

The suggested presentations are as tablets or powders (which can be dispersed in water) containing 300 mg each. Both these forms and the bulk compound are stable indefinitely under dry storage conditions.

Predicted cost per normal daily dose compared with some competitor drugs (based on use as analgesic):

AP1011	1p
Panadol	6p
Paracetamol	2p

AP1011 must be administered by mouth and can be formulated into tablets or as powder for dispersal in water.

Action AP1011 is hydrolysed in the stomach and small intestine to form an active compound which is absorbed through the intestinal wall into the bloodstream.

It acts by inhibiting the synthesis of prostaglandins (PGs). These are complex cyclic carboxylic acids and are identified by letter labels (PGE, PGF, etc.). They have many functions, among which are production of redness, heat, swelling and pain. Reductions in these symptoms are therefore experienced after taking the medicine. Some aspects of blood-clotting are also affected by prostaglandins, hence AP1011 is of use in inhibiting thrombosis.

Side-effects/contra-indications AP1011 appears effective and relatively safe in use. Long-term use does not lead to tolerance* or dependence†.

AP1011 has no effect on the central nervous system, liver or kidneys except in overdose. It can produce stomach bleeding, but this is in small amount and usually unnoticed by the patient (normal persons may experience slight stomach bleeding without taking the medicine).

0.2% of the population are intolerant of the compound and up to 28% of chronic asthma sufferers may have a bout of asthma brought on by using it.

Blood disorders such as anaemia can be caused in some patients, mainly as a result of blood loss. These cases recover on removal of the medicine and where essential symptoms may be controlled using iron tablets.

If taken during early pregnancy, AP1011 may induce abortion.

Cases of prolonged labour and excess bleeding in mother and baby at birth have been attributed to the medicine.

No tumour-inducing or carcinogenic effects related to the medicine have been observed.

The LD_{50} is estimated to be 1750 mg/kg of body weight.‡

Care should be taken when prescribing to patients already taking other medicines.

Symptoms of overdose are tinnitus (ringing in the ears), dizziness, confusion and respiratory problems.

AP1011 lowers blood-clotting ability and can produce longer bleeding times after wounds, but this effect is of benefit in the prevention of thrombosis.

* 'Tolerance' refers to the ability of the body to build up resistance to a compound so that larger and larger doses are needed to produce a given effect.

† Addiction to the compound.

‡ The toxicity of a compound is tested by finding the dose which will kill 50% of a trial group of animals (usually rats). The dose is measured in terms of the number of milligrams of compound per kilogram of body weight of the animal.

Second technological and economic appraisal

Technical information on compound H2202

H2202 is a mild sedative and hypnotic (sleep-inducing) drug. It fills the gap between mild pain-relieving sedatives such as paracetamol, and benzodiazepines like Valium and Mogadon which are addictive with prolonged use. H2202 is neither addictive nor toxic in overdose.

It is especially useful as a sedative during labour but can also be given to women who complain of nervousness, inability to sleep, or morning sickness during pregnancy. It also has more general uses for mild sleep induction.

Dose rate as a sedative is 25 mg up to three times a day.

As a hypnotic, dose rate is up to a maximum of 200 mg.

Manufacture, storage and distribution A satisfactory semi-technical scale production process has been established and no difficulty is foreseen in scaling this up for full production. The process is relatively simple, but the eventual cost of manufacture is estimated as about £35 per 100 g, mainly due to the cost of using manufactured chemicals as feedstocks.

H2202 is administered by mouth in tablet form. Normal tablet-forming equipment can be used to produce tablets in two presentations, containing either 25 mg or 100 mg of the active compound each.

Both the tablets and the bulk compound are stable in dry storage.

The principal competitors (e.g. Mogadon and Valium) are addictive. H2202 is non-addictive and has a substantially higher LD_{50}.*

Action H2202 is a white crystalline solid. It is hydrolysed in the body giving benzene-1,2-dicarboxylic acid, glutamic acid and ammonia. The mode of action in the body is not yet fully understood.

Side-effects/contra-indications In many patients there are no side-effects from small doses over short periods. Some patients experience one or more of the following side-effects: giddiness, nausea, shivering, constipation or symptoms similar to a 'hangover'. In a few cases effects on circulation are reported producing coldness or 'pins-and-needles' in hands or feet. These effects clear up on removal of the medicine.

At high dosage, disturbance of the central nervous system can take place and trembling is noticeable. Dosage over a long period can lead to polyneuritis, a nervous degeneration which is non-reversible. In pregnant women, H2202 can cross the placenta (the organ in the womb which provides the developing embryo with nutrients), hence there is a possible effect if the medicine is taken during the first two months of pregnancy.

* The toxicity of a compound is tested by finding the dose which will kill 50% of a trial group of animals (usually rats). The dose is measured in terms of the number of milligrams of compound per kilogram of body weight of the animal.

Technical and economic appraisal: management group briefing and evaluation report form

Attached to this form are reports from Research Division on compounds for which they have completed preliminary screening since our last meeting. Please produce an evaluation of the information for each of these and recommend suitability for further development and clinical trials, using the points which follow.

Compound under evaluation: .....

1 Activity

a What types of activity are already established?
What symptoms/illnesses/conditions may be treatable?
Is this likely to lead to a large market for the product?

b Are there indications of any other possible types of activity?
What additional uses might result from this?
Does this lead to a large additional potential market?

2 Manufacture, storage, delivery

a Manufacture: comment on likely costs and difficulty

b Stability: will it be possible to hold stocks for a reasonable period?

c Can the medicine be formulated in an attractive and convenient way?

d How will the likely cost compare with competitor medicines?

3 Contra-indications

a Known side-effects:

b Effects of overdose:

c LD_{50} calculated for average adults (body weight 65 kg)

d Are there any groups of people who should not use the medicine?

4 Risk/benefit ratio

a Do the benefits of using the medicine outweigh the side-effects for the large majority of those likely to use the medicine? (Circle the appropriate balance)
very good / good / acceptable / poor / very poor

5 Cost/benefit ratio

a How does the cost of the treatment compare with the value of its effects?
very good / good / acceptable / poor / very poor

6 Recommendation

a Should we proceed to clinical trials of this compound?

b If so, what special points will need to be evaluated?

c Please compare the potential of this compound with any other considered at this stage, and recommend an order of preference for development funding.

WM9

Check your notes on *What's in a Medicine?*

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

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

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

- Be able to recognise members of the following homologous series: phenols, acyl chlorides and esters.
- The use of systematic nomenclature to name carboxylic acids and esters.
- The acidic nature of carboxylic acids.
- The reactions of alcohols with carboxylic acids to form esters.
- The characteristic properties of phenols, including: acidic nature, test with iron(III) chloride solution, and reaction with acyl chlorides to form esters.
- The increasing relative strengths as acids of alcohols, phenols and carboxylic acids.
- The technique of heating under reflux for reactions involving volatile liquids (**Activity WM2**).
- The technique of thin-layer chromatography (t.l.c.) and the interpretation of results (**Activity WM2**).
- How the following forms of spectroscopy can be used for the elucidation of molecular structure: mass spectrometry (m.s.) and infrared spectroscopy (i.r.).
- The interpretation of mass spectra (molecular ion and significance of the fragmentation pattern) for salicylic acid and simple compounds containing a limited range of functional groups (hydroxyl, carbonyl, carboxylic acid and ester groups).
- The interpretation of infrared spectra for salicylic acid and simple compounds containing a limited range of functional groups (hydroxyl, carbonyl, carboxylic acid and ester groups).
- How more effective medicines can be obtained by modifying the structure of existing medicines (**Storyline WM5**).
- The procedures used in developing and establishing the safety of a medicine (**Storyline WM8** and **Activity WM8**).