

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 CO₂ and SiO₂ in terms of their different structures (**Activity M2.6**).

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:
- carbon monoxide?
 - silica?
 - 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.

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'.

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.

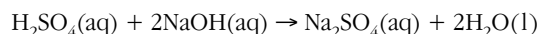
Unfortunately, many mining regions are naturally hotter than that, to say nothing of the heat generated by the process itself: the cost of reducing and holding the temperature to the required level can make the process forbiddingly expensive.

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.

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:



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

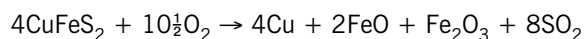
- 10 The titration flask contained 10.0 cm^3 of sulphuric acid solution. Calculate the amount (in moles) of acid which would be contained in 1 dm^3 (1000 cm^3) of solution. Write down the concentration of the sulphuric acid in units of mol dm^{-3} .

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:



- 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 $0.365 \text{ tonnes km}^{-3}$.
 - 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.

M2.4

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



CARE Eye protection must be worn.



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

E9 Transfer the remaining contents of your volumetric flask to a 250 cm³ conical flask and continue to step **10**.

- e**
- i** From the burette readings which agree to within 0.2 cm³, 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 Cu²⁺(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 Cu²⁺(aq) ions is the same as the amount (in moles) of sodium thiosulphate used.

- iii** Calculate the amount (in moles) of Cu²⁺(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 cm³ 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 cm³ portions of distilled water and twice with 10 cm³ 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?

- 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 cm³ 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 cm³ 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 cm³ conical flask using a conventional filter funnel.

Finding the concentration of Cu²⁺(aq) ions in solution (Optional extension)

E1 Transfer the filtrate to a 250 cm³ 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 cm³ of the solution and transfer it to a 100 cm³ 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 cm³ 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 cm³ 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.

Leaching the ore

- 1 Place about 50 g roasted ore in a 250 cm³ conical flask. Add 100 cm³ 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 cm³ 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, Cu²⁺ 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 cm³ 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 cm³ conical flask and a coarse filter paper.

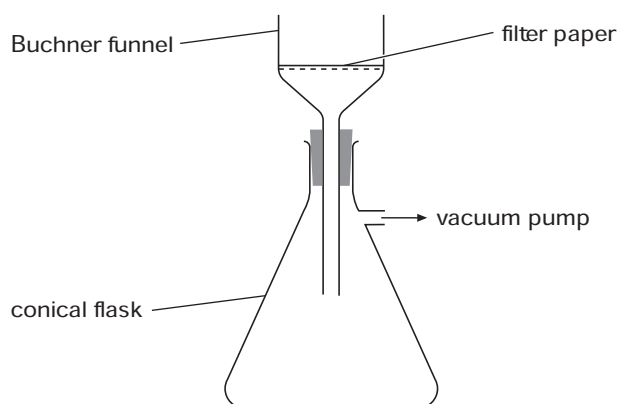


Figure 2 Diagram of a vacuum filtration assembly

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 cm³ 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 cm³ beaker.
- 7 Add a second 40 cm³ 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.

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 cm³ conical flask
- cottonwool
- ammonia leach solution – see **Activity M2.2** (100 cm³)
- 100 cm³ measuring cylinder
- domestic food-warming tray to use as a heating mat
- test-tubes
- apparatus for vacuum filtration (if available)
- 400 cm³ beaker
- 250 cm³ beaker
- sulphuric acid, 4 mol dm⁻³ (40 cm³)
- sodium hydroxide solution, 2 mol dm⁻³ (access to reagent bottle)
- Universal Indicator paper
- zinc dust (4 g)
- propanone (20 cm³)
- watch-glass
- glass rod
- access to balance
- access to fume cupboard
- filter funnels

ammonia solution



HARMFUL



CORROSIVE

propanone



HIGHLY FLAMMABLE

sodium hydroxide solution



CORROSIVE

sulphuric acid



CORROSIVE

CARE Eye protection must be worn.



WEAR EYE PROTECTION

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

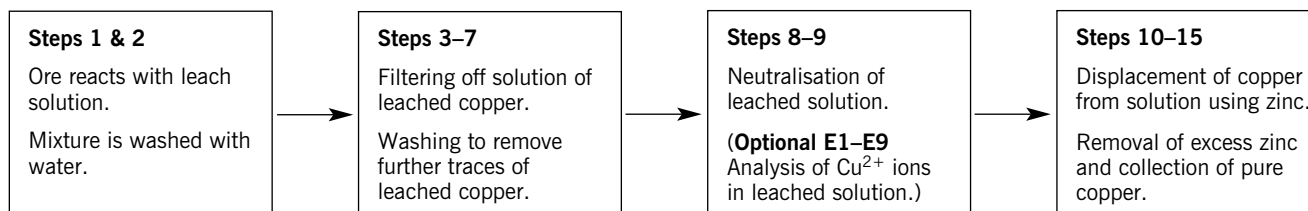
Additional requirements (optional)

- 250 cm³ volumetric flask
- 10.0 cm³ pipette
- pipette filler
- 100 cm³ conical flask
- burette
- ammonium ethanoate, solid (10 g)
- potassium iodide, solid (5 g)
- sodium thiosulphate solution, 0.100 mol dm⁻³ (50 cm³)
- freshly made starch solution (5 cm³)

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



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 cm³ beakers
- clingfilm or watch-glasses
- 10 cm³ measuring cylinder
- sample of roasted copper ore (6 g)
- hydrochloric acid, 50% (10 cm³)
- ammonia leach solution
 - 192 g ammonium carbonate dissolved in 1 dm³ of 4 mol dm⁻³ ammonia solution (10 cm³)
- 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



HARMFUL



CORROSIVE

hydrochloric acid



CORROSIVE

CARE Eye protection must be worn.



WEAR EYE PROTECTION

What you do

- 1 Put about 3 g of the roasted ore into each of two beakers. Add 10 cm³ of the hydrochloric acid (**CARE** Corrosive) to one beaker and cover it loosely with clingfilm or with a watch-glass.
- 2 Add 10 cm³ 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.

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 chalcopryite, 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*
chalcopryite, CuFeS_2	brassy yellow; metallic-looking
bornite, Cu_5FeS_4	red/brown with streaks of blue
malachite, $\text{Cu}_2(\text{OH})_2\text{CO}_3$	green; dull-stony looking
azurite, $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$	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.

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 ($\text{Na} \cdot x\text{H}_2\text{O}$)⁺, so some water is transferred, but the membrane is impermeable to free water molecules.

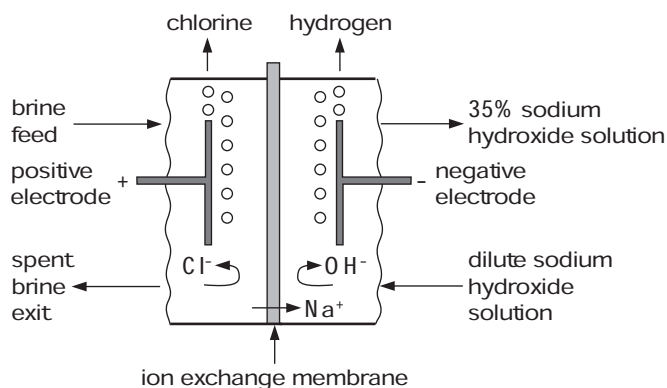


Figure 1 The membrane cell for the manufacture of chlorine, hydrogen and sodium hydroxide

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 $\text{Na}^+(\text{aq})$ ions
- impermeable to $\text{Cl}^-(\text{aq})$ and $\text{OH}^-(\text{aq})$ 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 ($-\text{COO}^-$) and sulphonate ($-\text{SO}_3^-$). These attract the positive sodium ions but repel negative ions like $\text{OH}^-(\text{aq})$. The $\text{Na}^+(\text{aq})$ 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.

- Explain why the membrane needs to be:
 - permeable to $\text{Na}^+(\text{aq})$ ions
 - impermeable to $\text{Cl}^-(\text{aq})$ and $\text{OH}^-(\text{aq})$ ions.
- Before it is used, the brine must be carefully purified to remove $\text{Ca}^{2+}(\text{aq})$ and $\text{Mg}^{2+}(\text{aq})$ ions. Suggest why this is necessary.
- Describe how well the membrane cell meets the ideal cell design criteria listed earlier.
- 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:
 - why the membrane cell may be preferred
 - why the mercury cells have not been replaced by membrane cells.
- 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.

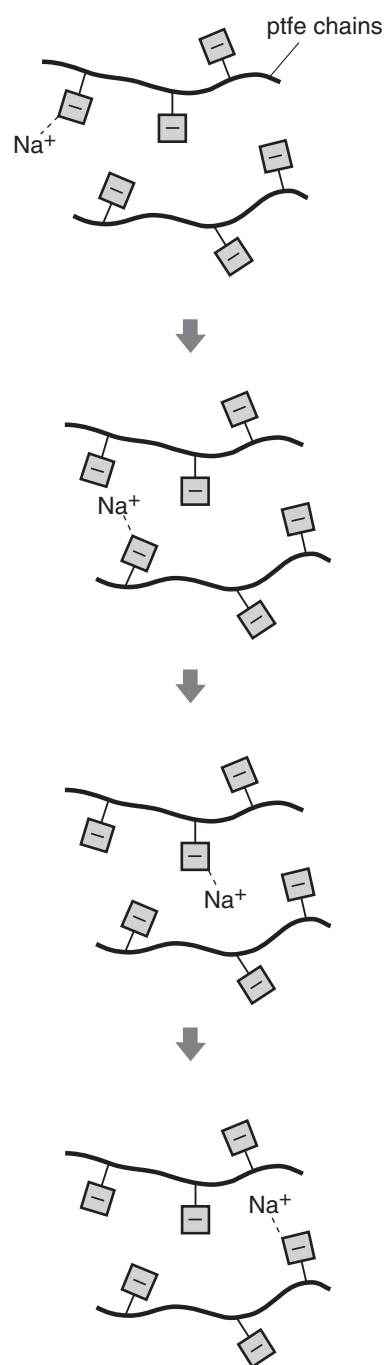


Figure 2 Sodium ions passing through a channel in an electrolysis cell membrane

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 electrolysis of 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: $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$

at the negative electrode: $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$

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

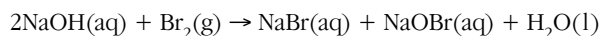
Any electrolysis cell used to make chlorine, hydrogen and sodium hydroxide by the electrolysis of sodium chloride solution must be designed to:

- 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.

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:



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.

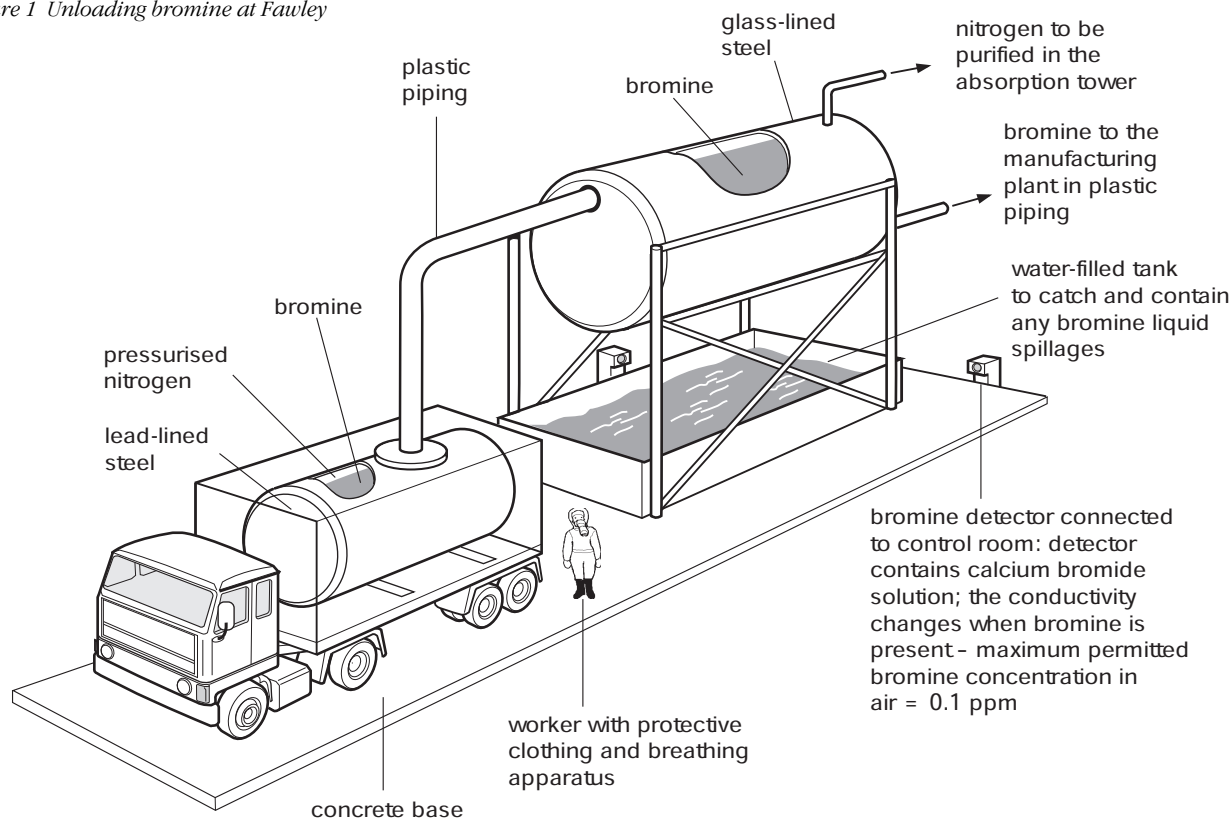
A pH meter is one of the other detectors used to monitor the efficiency of the absorption tower.

- 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.

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.)

- 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 cm³ 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, S₂O₃²⁻(aq). The reaction is often used in analysis. The products are iodide ions, I⁻(aq), and tetrathionate ions, S₄O₆²⁻(aq).
- i State the oxidation number of sulphur in:
 - S₂O₃²⁻
 - S₄O₆²⁻
 - ii Write a balanced equation for the reaction of iodine with thiosulphate ions.
 - iii Explain why this can be regarded as a redox reaction.

- 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 cm³.

Potassium chloride	Potassium bromide	Potassium iodide
state and colour		

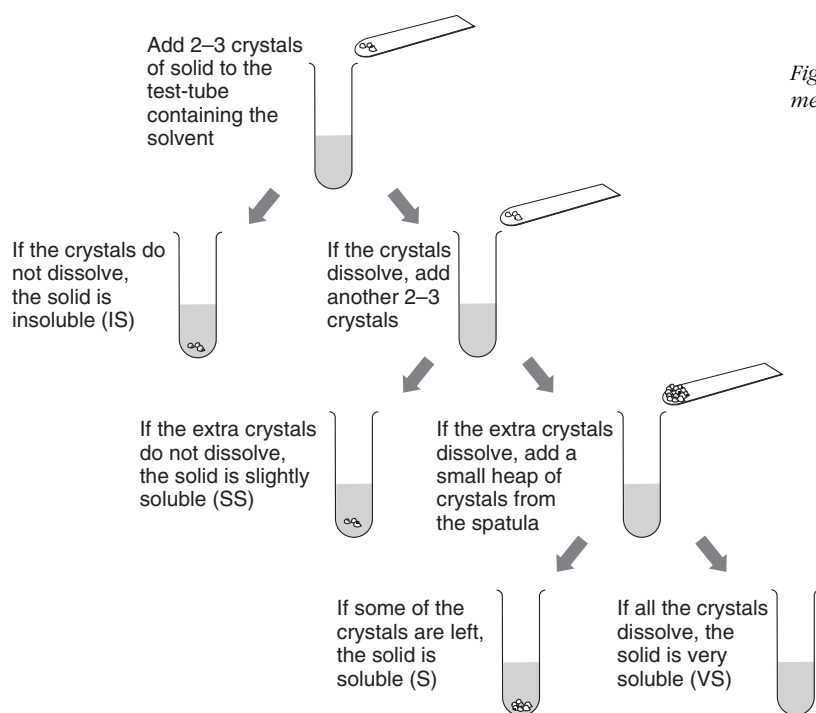


Figure 1 Key for investigating solubilities of alkali metal halides

QUESTIONS

- 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.
- 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







- 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.

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 cm³)
- bromine solution, in water (5 cm³)
- iodine solution, in water (5 cm³)
- 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 cm³)
- potassium bromide solution, 0.1 mol dm⁻³ (10 cm³)
- potassium iodide solution, 0.1 mol dm⁻³ (10 cm³)
- silver nitrate solution, 0.025 mol dm⁻³ (1 cm³)
- cyclohexane (30 cm³)

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

bromine solution		
	HARMFUL	IRRITANT
chlorine solution		
	HARMFUL	IRRITANT
cyclohexane		
	HIGHLY FLAMMABLE	
iodine solution		
	HARMFUL	

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 cm³ 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:

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.

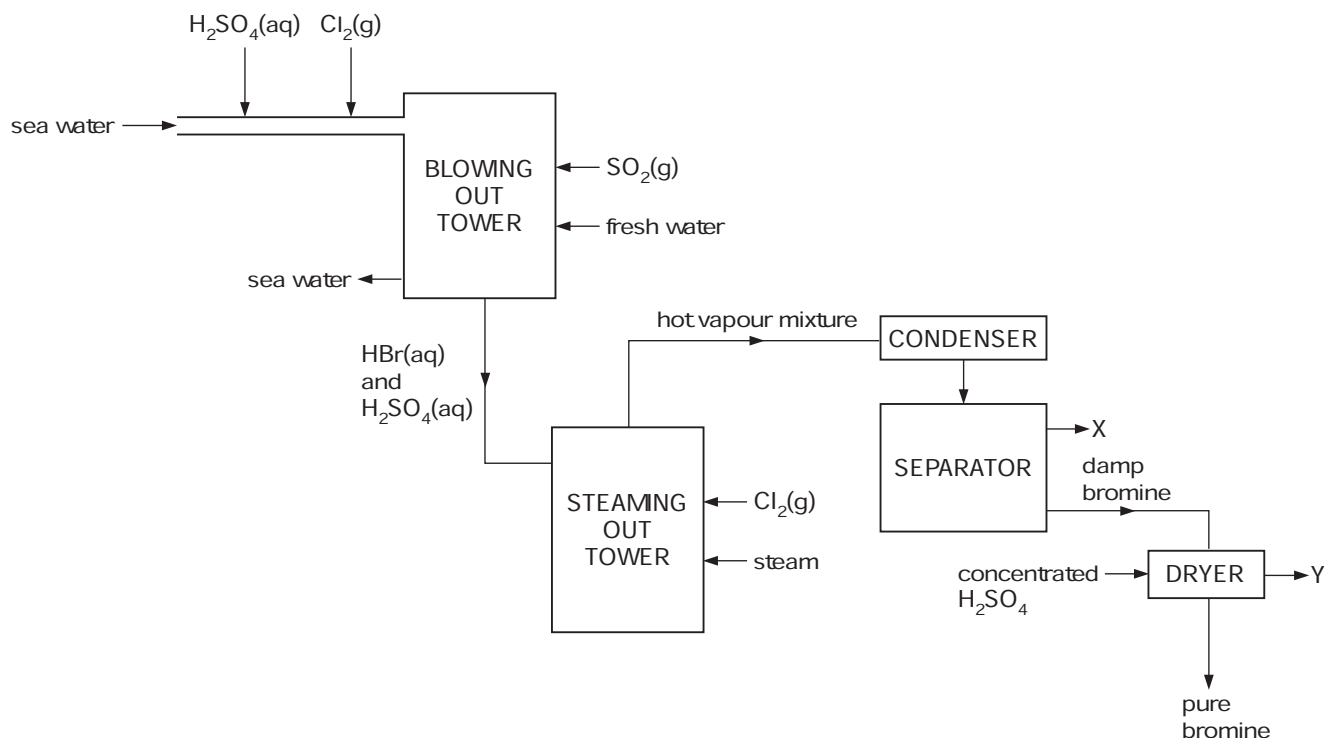


Figure 1 Flow diagram for bromine production at the Almuich works

QUESTIONS

- Write an equation, with state symbols, for the redox reaction occurring in:
 - the sea water inlet pipe
 - the blowing-out tower
 - the steaming-out tower.
 For each reaction identify what is oxidised and what is the oxidising agent.
- Which of the properties of bromine make it possible to separate it from water?
- What would you expect the *hot vapour mixture* leaving the steaming-out tower to contain?
- Suggest what the outputs would be at points X and Y.
- Identify a point on the flow diagram where:
 - heating is required
 - cooling is required.

Reagents	Observations	Explanation
i 1 cm ³ CuSO ₄ (aq) + 5 cm ³ H ₂ O	Blue solution becomes paler as water is added	Words used: diluting, mixing, solution
ii 5 drops CuSO ₄ (aq) + 5 cm ³ H ₂ O		
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 ₂ CO 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 ₂ CO 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 ₂ SO ₄ (aq)		

Table 1 Results table

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 $\text{Cu}^{2+}(\text{aq})$ ions in a 1 mol dm^{-3} solution of copper(II) sulphate?
- b** What is the concentration of $\text{SO}_4^{2-}(\text{aq})$ ions in a 1 mol dm^{-3} solution of copper(II) sulphate?
- c** What is the concentration of each of $\text{Cu}^{2+}(\text{aq})$ and $\text{Cl}^{-}(\text{aq})$ ions in a 1 mol dm^{-3} solution of copper(II) chloride, $\text{CuCl}_2(\text{aq})$?

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} $\text{NaOH}(\text{aq})$ reacts with
 1 dm^3 of 1 mol dm^{-3} $\text{HCl}(\text{aq})$
is the same as the enthalpy change when
 1 dm^3 of 1 mol dm^{-3} $\text{NaOH}(\text{aq})$ reacts with
 1 dm^3 of 1 mol dm^{-3} solution of $\text{HNO}_3(\text{aq})$.
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.

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

Requirements

- test-tubes
- teat pipettes
- 10 cm³ measuring cylinder
- copper(II) carbonate, solid (1 spatula measure)
- copper(II) sulphate solution, 1 mol dm⁻³ (6 cm³)
- sodium nitrate(V) solution, 1 mol dm⁻³ (10 cm³)
- sodium carbonate solution, 1 mol dm⁻³ (2 cm³)
- lead nitrate(V) solution, 1 mol dm⁻³ (3 cm³)
- potassium iodide solution, 1 mol dm⁻³ (1 cm³)
- hydrochloric acid, 1 mol dm⁻³ (3 cm³)
- sodium hydroxide solution, 1 mol dm⁻³ (2 cm³)
- sulphuric acid, 1 mol dm⁻³ (2 cm³)
- sodium chloride solution, 1 mol dm⁻³ (1 cm³)

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.