Cambridge OL

Chemistry

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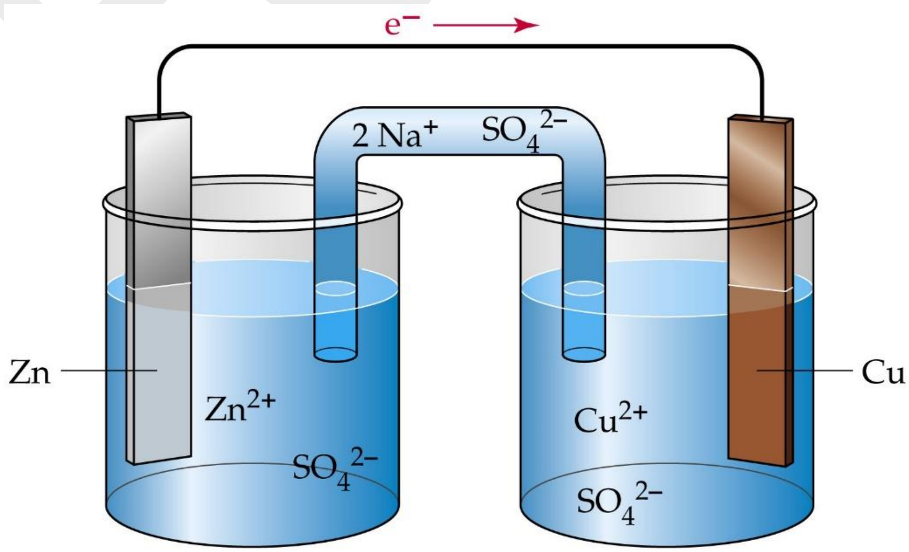
Chapter 05

Electrochemistry



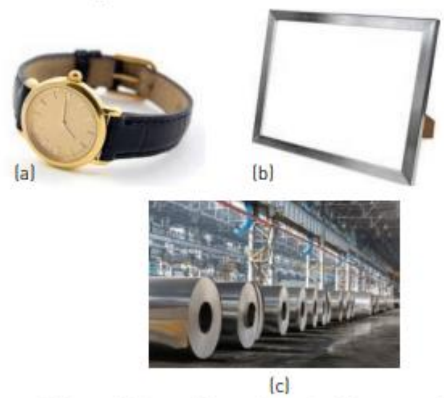
5.1 Electricity and chemistry

Electrolysis is the process of breaking down an ionic compound, either molten or in solution, by passing electricity through it, with the decomposed substance being an **electrolyte**, which conducts electricity.

The electricity is carried through the electrolyte by **ions**. In the molten state and in aqueous or water solution, the ions are free to move to the appropriate electrodes due to weakened forces of attraction between them.

» Substances that do not conduct electricity when in the molten state or in solution are called non-electrolytes.

» Substances that conduct electricity to a small extent in the molten state or in solution are called weak electrolytes.



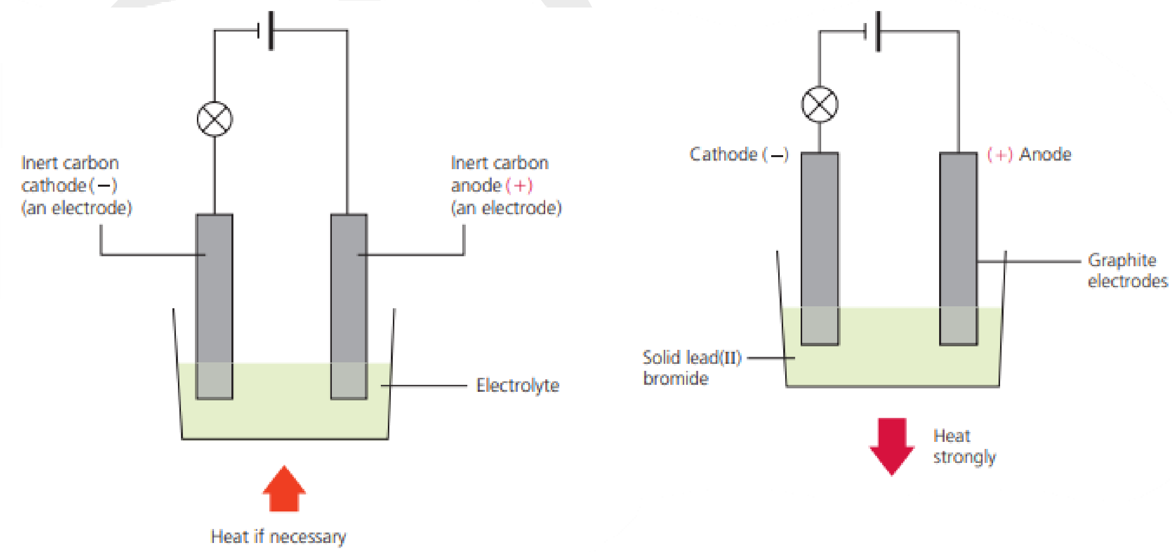
a This watch has a thin coating of gold over steel; the thin coating is produced by electrolysis
b This picture frame has been silver plated using an electroplating process involving electrolysis
c Aluminium is produced by electrolysis

▲ **Figure 5.1**

Key definitions
Electrolysis is the decomposition of an ionic compound, when molten or in aqueous solution, by the passage of an electric current.

The electric current enters and leaves the electrolyte through **electrodes**, which are usually made of unreactive metals, such as platinum or the non-metal carbon (graphite). These are said to be **inert electrodes** because they do not react with the products of electrolysis. The two electrodes are the **cathode**, the negative electrode which attracts **cations** (positively charged ions), and the **anode**, the positive electrode which attracts **anions** (negatively charged ions).

Metals or hydrogen are formed at the cathode and non-metals (other than hydrogen) are formed at the anode.



▲ **Figure 5.2** The important terms used in electrolysis

In the example of electrolysis of molten lead(II) bromide you will see that the transfer of charge during electrolysis is by:

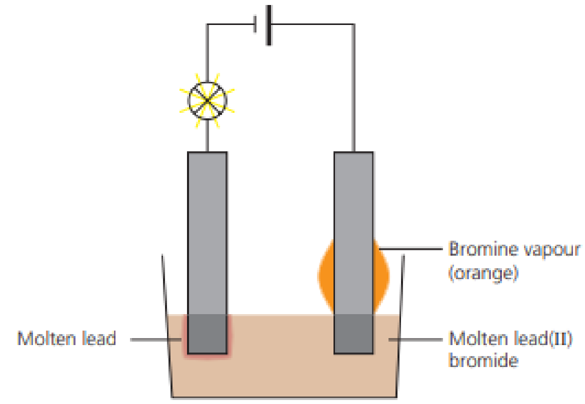
» The movement of electrons in the metallic or graphite electrodes

» The loss or gain of electrons from the external circuit at the electrodes
» The movement of ions in the electrolyte. The conduction that takes place in the electrodes is due to the movement of delocalised electrons (p. 46), whereas in the electrolyte the charge carriers are ions.

5.2 Electrolysis of lead (II) bromide (teacher demonstration)

This experiment should only ever be carried out as a teacher demonstration and in a fume cupboard.

Figure 5.3 shows solid lead(II) bromide (PbBr2) in a crucible with carbon electrodes. When heated, it becomes an electrolyte, producing lead metal at the cathode. This **binary compound**, which contains two chemically combined elements, breaks down into its constituent elements when exposed to an electric current, forming metals like lead and non-metals like bromine.



▲ **Figure 5.3** The electrolysis of molten lead(II) bromide

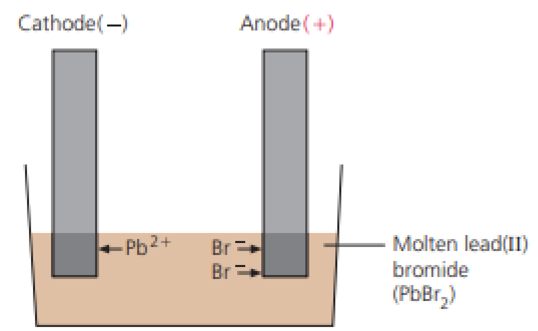
molten lead(II) bromide → bromine + lead

$PbBr_2(l) \rightarrow Br_2(g) + Pb(l)$

To produce lead metal atoms, these lead ions must each collect two electrons at the cathode:

lead ion + electrons → lead atom

$Pb^{2+}(l) + 2e^- \rightarrow Pb(l)$



▲ **Figure 5.4** The lead ions (Pb^{2+}) are attracted to the cathode and the bromide ions (Br^-) are attracted to the anode

Reduction is the process of gaining electrons, with chemical equations like lead production at the cathode and anode being ionic half-equations. Bromine molecules form when each ion moves to the anode and loses its negative charge.

bromide ion → bromine atom + electron

$Br^-(l) \rightarrow Br + e^-$

Two bromine atoms then combine to form a bromine molecule:

bromine atoms → bromine molecule

$2Br \rightarrow Br_2(g)$

5.3 Electrolysis of aluminum oxide

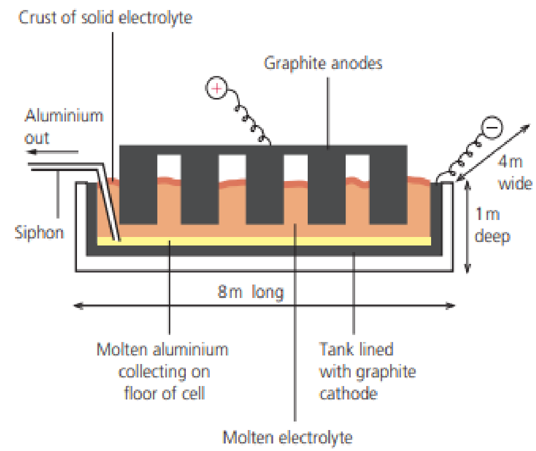
The main **ore** of aluminium, bauxite, is extracted through electrolysis, a method challenging due to its reactive nature, as many elements are tightly bound to their combined form.

Today we use aluminium in very large quantities. The commercial extraction of aluminium involves the following stages.

» Bauxite, an impure form of aluminium oxide, is first treated to obtain pure aluminium oxide. This improves the conductivity of the molten aluminium oxide.

» Cryolite, a natural mineral found in Greenland, dissolves purified aluminium oxide, reducing the electrolysis cell's working temperature from 2017°C to 800-1000°C, significantly reducing energy requirements.

» The molten mixture is then electrolysed in a cell similar to that shown in Figure 5.6.



▲ **Figure 5.6** The cell is used in industry to extract aluminium by electrolysis

This process involves lowering graphite blocks into molten mixture, with the cathode being the steel vessel's graphite lining. Melting aluminum oxide ions breaks electrostatic forces, causing oxidation and negatively charged oxide ions attracted to the positive electrode.

oxide ions → oxygen molecules + electrons

$$2O^{2-}(l) \rightarrow O_2(g) + 4e^-$$

The positive aluminium ions are attracted to the cathode (the negative electrode). They gain electrons to form molten aluminium metal (reduction).

aluminium ions → electrons + aluminium metal

$$Al^{3+}(l) \rightarrow 3e^- + Al(l)$$

A handy way of remembering what happens is **OIL RIG** – **O**xidation **I**s **L**oss, **R**eduction **I**s **G**ain of electrons. The overall reaction which takes place in the cell is:

$$\text{aluminium oxide} \xrightarrow{\text{electrolysis}} \text{aluminium} + \text{oxygen}$$

$$2Al_2O_3(l) \rightarrow 4Al(l) + 3O_2(g)$$

The cell's bottom accumulates molten aluminium, which is periodically removed. No other metals are deposited, but graphite anodes produce carbon dioxide when oxygen is released.

carbon + oxygen → carbon dioxide

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

The electrolysis of aluminium oxide requires large amounts of electricity, making it an economic process. Hydroelectric power (HEP) is typically used to provide some of the required energy.

Aluminium, the second most widely used metal after iron, is produced in large quantities due to cheap electrical energy. Its low density, chemical inertness, and good electrical conductivity make it suitable for making electrical/transmission cables, cars, bikes, cooking foil, food containers, and alloys like duralumin.

▲ **Figure 5.7** An aluminium smelting plant

There are serious environmental problems associated with the location of aluminium plants including:

» The effects of the extracted impurities, which form a red mud (Figure 5.9)

» The fine cryolite dust, which is emitted through very tall chimneys so as not to affect the surrounding area

» They claimed link between environmental aluminium and a degenerative brain disorder called Alzheimer's disease.

▲ **Figure 5.9** Pollution from bauxite mining in Malaysia

▲ **Figure 5.8** Aluminium is used in the manufacture of aeroplane bodies

5.4 Electrolysis of aqueous solutions

Other industrial processes involve the electrolysis of aqueous solutions. To explain what is happening in these processes, we will first consider the electrolysis of dilute sulfuric acid.

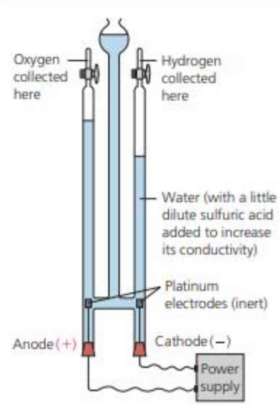
Electrolysis of dilute sulfuric acid

Pure water is a very poor conductor of electricity because there are so few ions in it. However, it can be made to decompose if an electric current is passed through it in a Hofmann voltameter, as in Figure 5.11.

Water conducts electricity better when a solution of sulfuric acid or sodium hydroxide is added. Electric current flows through the solution, producing gases at two electrodes and collected in side arms. After 20 minutes, twice as much gas is produced at the cathode, indicating hydrogen gas.

hydrogen ions + electrons → hydrogen molecules

$$4H^+(aq) \quad + \quad 4e^- \quad \rightarrow \quad 2H_2(g)$$



▲ **Figure 5.11** A Hofmann voltameter used to electrolyse water

The process involves losing H+(aq) in water molecules, resulting in hydroxide ions, OH−(aq), attracted to an anode, producing a glowing splint of oxygen.

hydroxide ions → water + oxygen + electrons

$$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$$

Sir Humphry Davy's experiment confirmed water's formula as H2O. In dilute sulfuric acid electrolysis, platinum can be replaced by graphite, producing oxygen and carbon dioxide at the anode, with carbon dioxide also formed.

Electrolysis of concentrated aqueous sodium chloride

Dissolving sodium chloride in water allows ions to move, producing hydrogen and chlorine when electrolyzed, despite the expected sodium production at the cathode.

Four ions are present in the solution:
» From water: H+ and OH−
» From sodium chloride: Na+ and Cl−

H+ and Na+ ions are attracted to the cathode, with H+ ions accepting electrons more easily than Na+ ions, resulting in the production of hydrogen gas (H2).

hydrogen ions + electrons $\xrightarrow{\text{reduction}}$ hydrogen molecules

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

The electrolysis of aqueous solutions typically doesn't form highly reactive metals like sodium at the cathode, as they release hydrogen when reacting with water, releasing more electrons than OH− ions.

chloride ions $\xrightarrow{\text{oxidation}}$ chlorine molecules + electrons

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

This leaves a high concentration of hydroxide ions, OH−(aq), around the cathode. The solution in the region of the anode therefore becomes alkaline.

Electrolysis guidelines

The following points may help you work out the products of electrolysis in unfamiliar situations. They will also help you remember what happens at each electrode.

» Non-metals are produced at the anode whereas metals and hydrogen gas are produced at the cathode.

» At an inert anode, chlorine, bromine and iodine (the halogens) are produced in preference to oxygen.

» At an inert cathode, hydrogen is produced in preference to metals unless unreactive metals such as copper are present.

5.5 Electrolysis of copper(II) sulfate aqueous solution

When the solution is electrolysed, oxygen gas and copper metal are formed at the anode and cathode respectively. Four ions are present in solution:

- from the water: $H^+(aq) + OH^-(aq)$
- from the copper(II) sulfate: $Cu^{2+}(aq) + SO_4^{2-}(aq)$

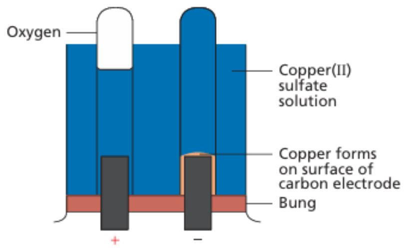


Figure 5.13 The electrolysis of copper(II) sulfate solution using inert electrodes

H+(aq) and Cu2+(aq) ions are both attracted to the cathode, the Cu2+ ions accepting electrons more readily than the H+ ions (preferential discharge). Copper metal is therefore deposited at the cathode (Figure 5.13).

copper ions + electrons → copper atoms

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

OH−(aq) and SO_4^{2-} (aq) ions are both attracted to the anode. The OH− ions release electrons more easily than the SO_4^{2-} ions, so oxygen gas and water are produced at the anode (Figure 5.14).

hydroxide ions → oxygen + water + electrons

$$4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^-$$

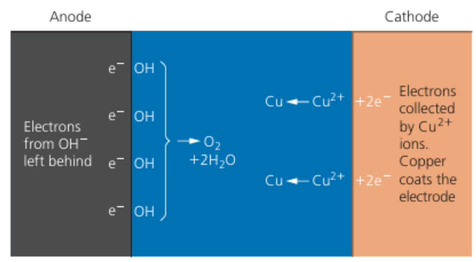
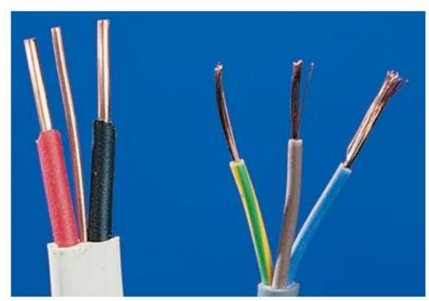


Figure 5.14 Oxygen is given off at the anode and copper is deposited at the cathode

Purification of copper

As copper is a very good conductor of electricity, it is used for electrical wiring and cables (Figure 5.15). Pure copper is also used in the manufacture of cooking utensils owing to its high thermal conductivity.

To ensure high conductivity in wires and cables, copper must be 99.99% pure. This is achieved through electrolysis, where impure copper serves as the anode and a cathode, both made from very pure copper. The electrolyte is a solution of copper(II) sulfate acidified with sulfuric acid.



a The copper used in electrical wiring has to be very pure

b Due to the high density of copper and its cost, steel-cored aluminium cables are used for electrical transmission through national grids

Figure 5.15

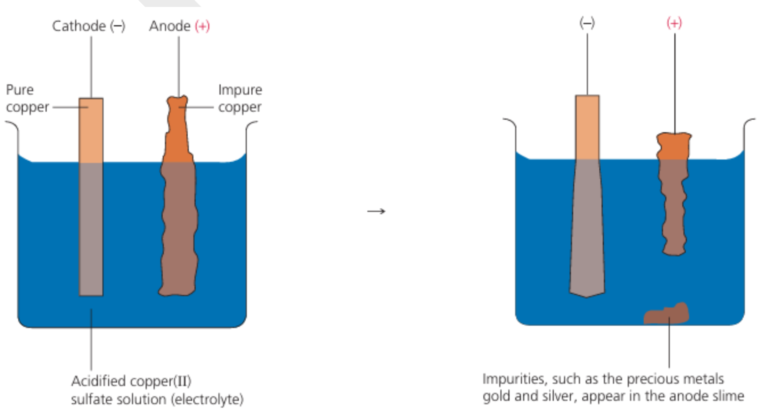
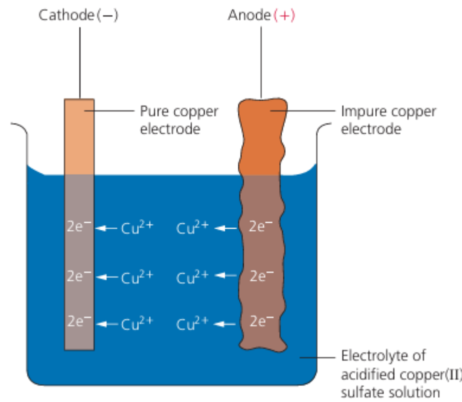


Figure 5.16 Copper purification process

Copper moves from an impure anode to pure cathode, collecting impurities in a slime. Recovery of precious metals is crucial for economics. Electrolysis takes three weeks, reducing anodes to 10% and cathodes to 100-120 kg. 0.25 V potential and 200 A/m^2 current density are used.



▲ **Figure 5.17** The movement of ions in the purification of copper by electrolysis

The ions present in the solution are:

- from the water: $H^+(aq) + OH^-(aq)$
- from the copper(II) sulfate: $Cu^{2+}(aq) + SO_4^{2-}(aq)$

because the copper atoms lose electrons and become copper ions, Cu2+(aq) (Figure 5.17).

copper atoms → copper ions + electrons

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

5.6 Fuel cells

Sir William Grove discovered the **fuel cell** principle in 1839, which converts chemical energy into electrical energy using hydrogen and oxygen reagents.

▲ **Figure 5.18** Fuel cell electric vehicles are being developed and may replace petrol and diesel engines

Key definition

A hydrogen–oxygen **fuel cell** uses hydrogen and oxygen to produce electricity with water as the only substance produced.

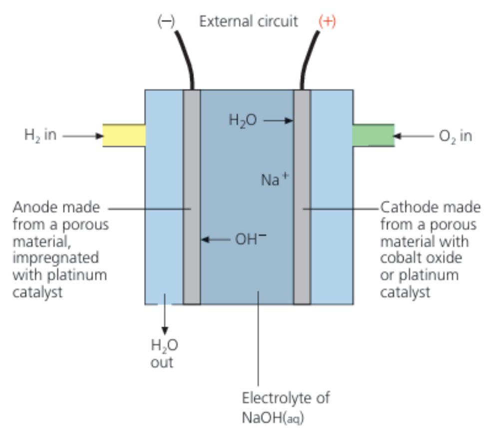
The aqueous NaOH electrolyte is kept within the cell by electrodes which are porous, allowing the transfer of O_2 , H_2 and water through them (Figure 5.19). As O_2 gas is passed into the cathode region of the cell it is reduced:

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

The OH^- ions formed are removed from the fuel cell by reaction with H_2:

$$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$$

The electrons produced by this process pass around an external circuit to the cathode.



▲ **Figure 5.19** A diagrammatic view of a fuel cell

Advantages and disadvantages of the hydrogen fuel cell

Fuel cell technology has its advantages.

» Uses hydrogen and oxygen and makes nonpolluting water in the process of generating electricity, whereas petrol and diesel engines produce many pollutants

» Is similar to a battery but does not require any external charging

» Is capable of producing electricity as long as hydrogen fuel and oxygen are supplied.

However, there are some disadvantages to using fuel cells. For example:

» Hydrogen is in the gas state at room temperature and pressure, so it is difficult to store in a car

» The infrastructure does not yet exist, as it does for fossil fuels, for example, the number of refuelling stations

» Fuel cells and electric motors are less durable than petrol or diesel engines, which means they do not last as long

» Fuel cells are very expensive at the moment.

5.7 Electroplating

Key definition

Electroplating is applied to metals to improve their appearance and resistance to corrosion.

Electroplating is the process involving electrolysis where one metal is plated, or coated, with another. Often the purpose of electroplating is to improve the appearance of the object and give a protective coating to the metal beneath.

The electroplating process is carried out in a cell such as the one shown in Figure 5.21a. This is often known as the 'plating bath' and it contains a suitable electrolyte, usually a solution of a metal salt.

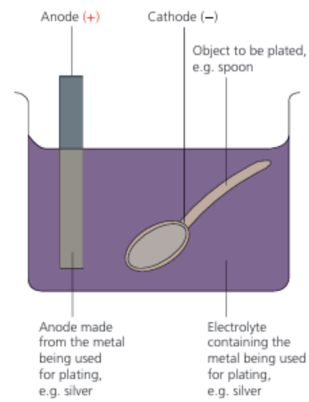
For silver plating the electrolyte is a solution of a silver salt. The item to be plated is made the cathode in the cell so that the metal ions move to it when the current is switched on.

The cathode reaction in this process is:

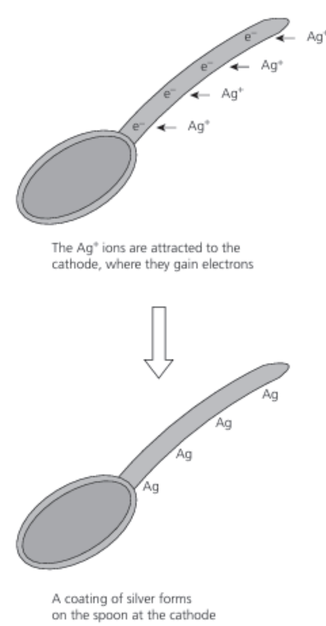
$$\text{silver ions} + \text{electrons} \rightarrow \text{silver atoms}$$

$$Ag^{+}(aq) \quad + \quad e^{-} \quad \rightarrow \quad Ag(s)$$

▲ **Figure 5.20** This tap has been chromium plated



a Silver plating a spoon



b Explaining silver plating

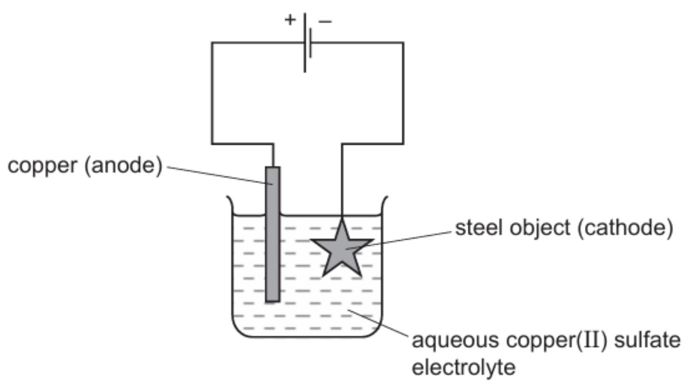
▲ **Figure 5.21**

Revision questions

1) Electroplating steel objects with silver involves a three-step process.

Step 1 A coating of copper is applied to the object.
Step 2 A coating of nickel is applied to the object.
Step 3 The coating of silver is applied to the object.

(a) A diagram of the apparatus used for step 1 is shown



(i) The chemical process taking place on the surface of the object is

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$

Explain whether this process is oxidation or reduction.

(ii) Explain why the concentration of copper ions in the electrolyte remains constant throughout step 1.
(b) Give two changes which would be needed in order to coat nickel onto the object in step 2
(c) Copper, nickel and silver are transition elements. Typical physical properties of transition elements are a high density and a high melting point.

Give three different properties of transition metals which are not typical of other metals

2) Chemical reactions are always accompanied by an energy change.

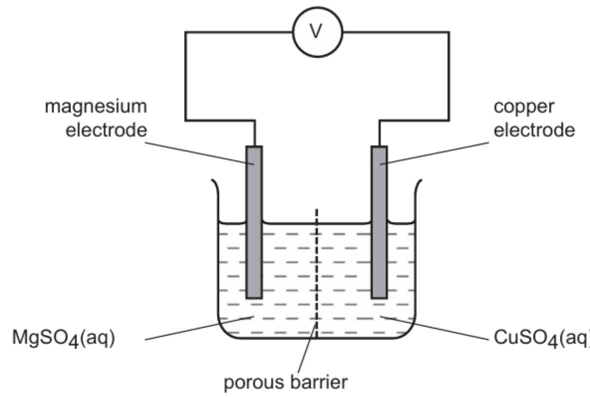
(a) Aluminium is extracted by the electrolysis of a molten mixture which contains aluminium oxide, Al 2O3. This decomposes to form aluminium at the negative electrode and oxygen at the positive electrode.

(i) W rite an ionic equation for the reaction at the negative electrode.
....

(ii) Complete the ionic equation for the reaction at the positive electrode.

(iii) Is the reaction exothermic or endothermic? Explain your answer.

(b) The cell shown below can be used to determine the order of reactivity of metals.



(i) Is the reaction in the cell exothermic or endothermic? Explain your answer.

(ii) Explain why the mass of the magnesium electrode decreases and the mass of the copper electrode increases

(iii) How could you use this cell to determine which is the more reactive metal, magnesium or manganese?

3) Zinc is an important metal. Its uses include making alloys and the construction of dry cells (batteries).

(a) Name an alloy which contains zinc. What is the other metal in this alloy?

(b) The main ore of zinc is zinc blende, ZnS.

(i) The ore is heated in the presence of air to form zinc oxide and sulfur dioxide. W rite the equation for this reaction.

(ii) Give a major use of sulfur dioxide.

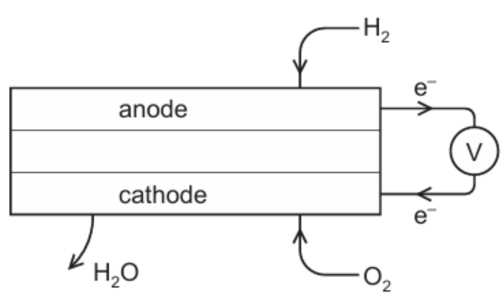
(c) Zinc can be obtained from zinc oxide in a two step process. Aqueous zinc sulfate is made from zinc oxide and then this solution is electrolysed with inert electrodes. The electrolysis is similar to that of copper(II) sulfate with inert electrodes.

(i) Name the reagent which will react with zinc oxide to form zinc sulfate.

(ii) Complete the following for the electrolysis of aqueous zinc sulfate. W rite the equation for the reaction at the negative electrode. ....

Name the product at the positive electrode

4) A fuel cell produces electrical energy by the oxidation of a fuel by oxygen. The fuel is usually hydrogen, but methane and methanol are two other fuels which may be used. A diagram of a hydrogen fuel cell is given below



(a) When the fuel is hydrogen, the only product is water. What additional product would be formed if methane was used?

(b) Write the equation for the chemical reaction that takes place in a hydrogen fuel cell.

(c) At which electrode does oxidation occur? Explain your choice.
(ii) Write an ionic equation for the reaction at this electrode.
(d) Fuel cells are used to propel cars. Give two advantages of a fuel cell over a gasoline-fuelled engine.

5) Carbonyl chloride is made from carbon monoxide and chlorine

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

(a) T wo methods of preparing carbon monoxide are from methane and oxygen, and from methane and steam.

(i) The reaction between methane and oxygen can also form carbon dioxide. How can carbon monoxide be made instead of carbon dioxide?

(ii) The following reaction is used to make carbon monoxide and hydrogen. The reaction is carried out at 1100 °C and normal pressure.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

The reaction is reversible and comes to equilibrium. Suggest why a high temperature is used.

(iii) What is the disadvantage of using a high pressure for the reaction given in (a)(ii)?

(b) Chlorine is made by the electrolysis of concentrated aqueous sodium chloride. Describe this electrolysis. Write ionic equations for the reactions at the electrodes and name the sodium compound formed.

6) At present the most important method of manufacturing hydrogen is steam reforming of methane.

(a) In the first stage of the process, methane reacts with steam at 800 °C.

$$CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g)$$

In the second stage of the process, carbon monoxide reacts with steam at 200 °C

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

(i) Explain why the position of equilibrium in the first reaction is affected by pressure but the position of equilibrium in the second reaction is not.

(ii) Suggest why a high temperature is needed in the first reaction to get a high yield of products but in the second reaction a high yield is obtained at a low temperature.

(b) Two other ways of producing hydrogen are cracking and electrolysis.

(i) Hydrogen can be a product of the cracking of long chain alkanes. Complete the equation for the cracking of C_8H_{18} .

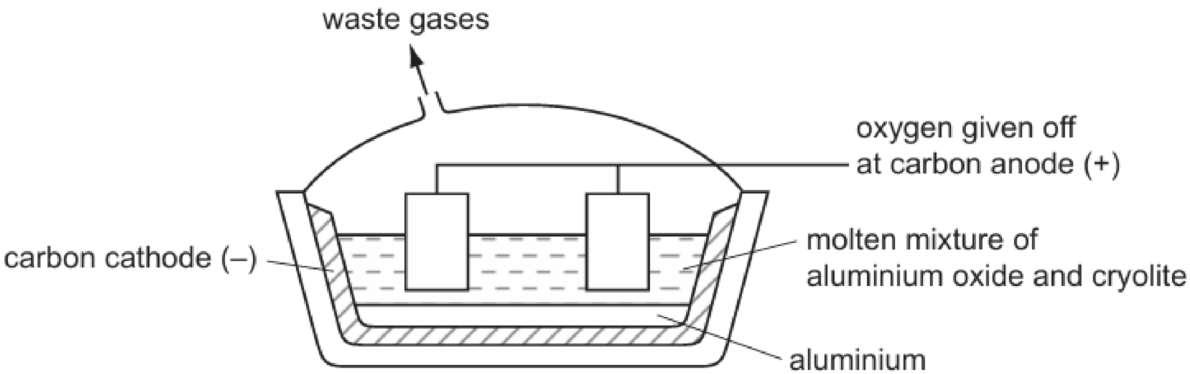
$$C_8H_{18} \rightarrow 2............ + H_2$$

(ii) There are three products of the electrolysis of concentrated aqueous sodium chloride. Hydrogen is one of them. Write an equation for the electrode reaction which forms hydrogen.

(iii) Name the other two products of the electrolysis of concentrated aqueous sodium chloride and give a use of each one.

7) Aluminium is an important metal with a wide range of uses.

(a) Aluminium is obtained by the electrolysis of aluminium oxide dissolved in molten cryolite



(i) Solid aluminium oxide is a poor conductor of electricity. It conducts either when molten or when dissolved in molten cryolite. Explain why.

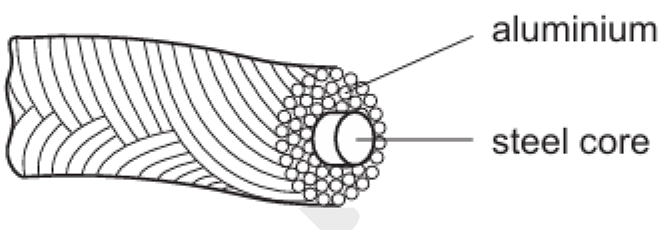
(ii) Why is a solution of aluminium oxide in molten cryolite used rather than molten aluminium oxide?

(iii) Explain why the carbon anodes need to be replaced periodically.

(iv) One reason why graphite is used for the electrodes is that it is a good conductor of electricity. Give another reason.

(b) Aluminium is used to make food containers because it resists corrosion. Explain why it is not attacked by the acids in food.

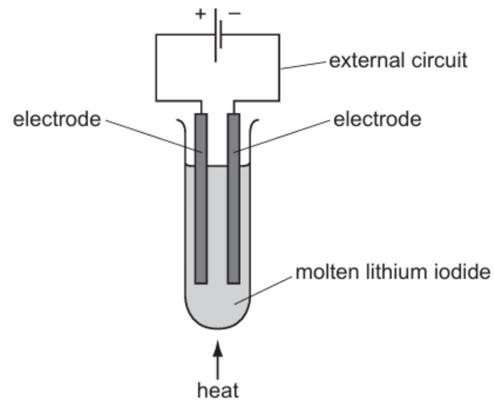
(c) Aluminium is used for overhead power (electricity) cables which usually have a steel core.



(i) Give two properties of aluminium which make it suitable for this use.

(ii) Explain why the cables have a steel core.

8) During electrolysis, ions move in the electrolyte and electrons move in the external circuit. Reactions occur at the electrodes.



(a) The diagram shows the electrolysis of molten lithium iodide.

(i) Draw an arrow on the diagram to show the direction of the electron flow in the external circuit.

(ii) Electrons are supplied to the external circuit. How and where is this done?

(iii) Explain why solid lithium iodide does not conduct electricity but when molten it is a good conductor.

(b) The results of experiments on electrolysis are shown in the following table. Complete the table. The first line has been done as an example.

electrolyte	electrodes	product at cathode	product at anode	change to electrolyte
molten lithium iodide	carbon	lithium	iodine	used up
aqueous copper(II) sulfate	platinum		oxygen	
concentrated aqueous potassium chloride	carbon		chlorine	

9) Tin is an element in Group IV.

(a) The position of tin in the reactivity series is:

zinc
iron
tin
copper

(i) For each of the following, decide if a reaction would occur. If there is a reaction, complete the equation, otherwise write 'no reaction'.

$Cu + Sn^{2+} \rightarrow$ ....

$Fe + Sn^{2+} \rightarrow$ ....

$Sn + Zn^{2+} \rightarrow$ ....

(ii) Name the three products formed when tin (II) nitrate is heated.

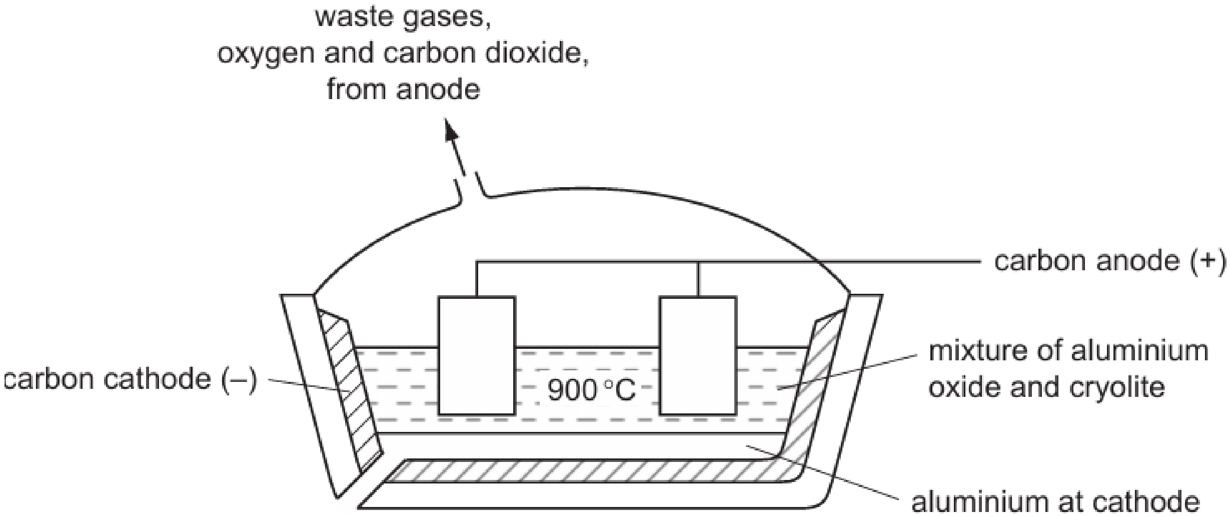
(b) Aqueous tin(II) sulfate is electrolysed using carbon electrodes. This electrolysis is similar to that of aqueous copper(II) sulfate using carbon electrodes.

(i) What is the product at the negative electrode (cathode)?

(ii) Write the equation for the reaction at the positive electrode (anode).

(iii) Name the acid formed in this electrolysis.

10) Aluminium is extracted by the electrolysis of a molten mixture of alumina, which is aluminium oxide, and cryolite.



(a) a) Alumina is obtained from the main ore of aluminium. Name this ore.

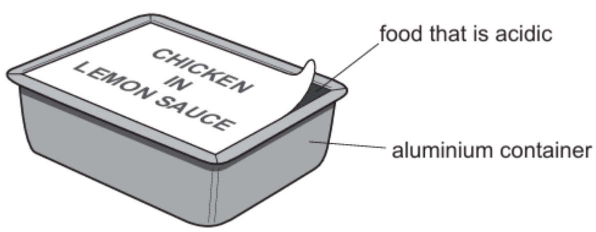
(ii) Explain why it is necessary to use a mixture, alumina and cryolite, rather than just alumina.

(iii) Copper can be extracted by the electrolysis of an aqueous solution. Suggest why the electrolysis of an aqueous solution cannot be used to extract aluminium.

(b) The ions which are involved in the electrolysis are Al^{3+} and O^{2-}. The products of this electrolysis are given on the diagram. Explain how they are formed. Use equations where appropriate.

(c) The uses of a metal are determined by its properties.

(i) Foods which are acidic can be supplied in aluminium containers.



Explain why the acid in the food does not react with the aluminium.

(ii) Explain why overhead electrical power cables are made from aluminium with a steel core.