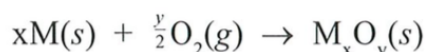# Corrosion as an oxidation process

The corrosion of metals costs Australia about three billion dollars annually. Much of this could be saved by a better understanding of the process and the application of appropriate preventative measures. The products of corrosion often have the same composition as common metal ores because corrosion is the reverse of metal extraction. In metal extraction a metal in an oxidised form is reduced to its elemental state. Corrosion involves the oxidation of a metal.

The best known form of corrosion is the rusting of iron, but most metals are susceptible to corrosion to some extent. In normal atmospheric conditions most metals form a microscopic surface film of oxide by reaction with oxygen.

$$xM(s) + \tfrac{y}{2}O_2(g) \rightarrow M_xO_y(s)$$

This layer usually adheres strongly to the metal and is finely grained. This makes it impervious to oxygen and thus protects the underlying metal from further oxidation. This is why reactive metals such as magnesium and aluminium do not corrode very rapidly in air. In the case of iron, the oxide layer is relatively porous and allows iron atoms to migrate through it to react further with oxygen of the air. This enables the corrosion of iron to continue.

Many non-corrosive alloys of iron such as stainless steel are effective in resisting rusting. This is because the alloying metals form a protective oxide layer at the surface. This oxide layer protects the surface iron atoms. Chromium is commonly used in stainless steels for this reason.

Common forms of corrosion, including the rusting of iron, usually involve an aqueous environment. The process may occur in solution or in a humid atmospheric environment. In all cases the 'wet' corrosion of metals has an electrochemical nature.

Rusting is undesirable for many reasons other than the sheer loss of steel. Corroded structures such as bridges, buildings, cars and machinery are weakened and become dangerous. Electrical connections often corrode and the corrosion products reduce proper contact between terminals and leads. Similarly, corroded fittings such as lids, nuts and bolts, taps, valves and hinges often jam as corrosion products swell and fill the space between moving parts. Tanks, pipes and car radiators may leak as corrosion creates holes in the metal walls.

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Figure 19.14
If the copper(II) sulfate solution in a Daniell cell is replaced by aerated sodium chloride solution, the cathode reaction is the reduction of oxygen.
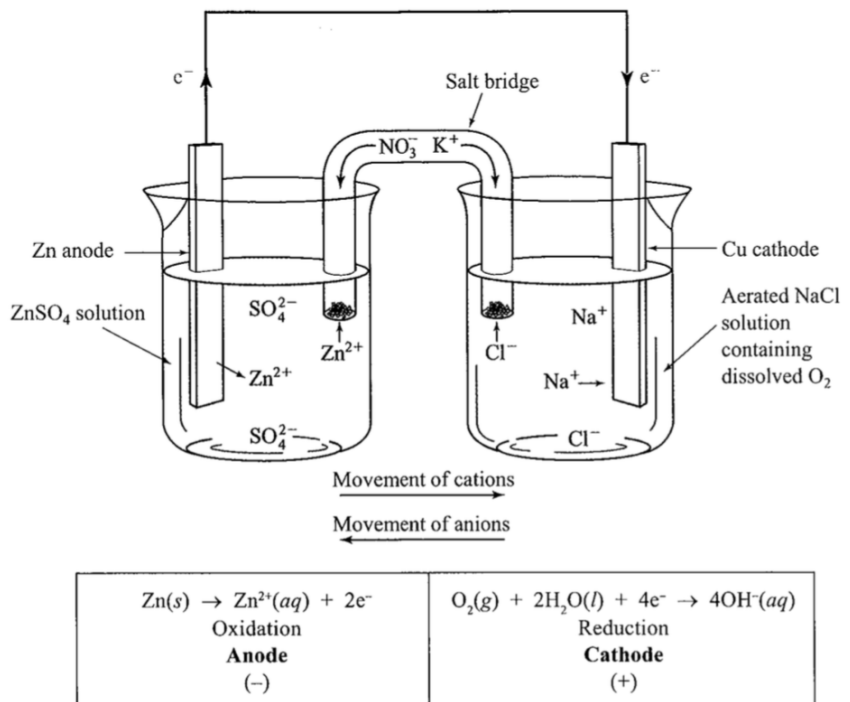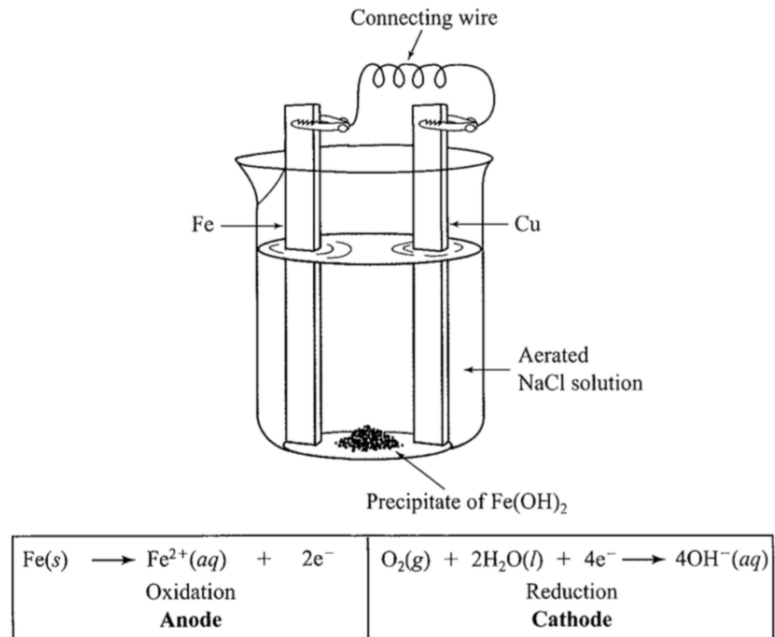

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
Oxidation	Reduction
Anode	**Cathode**
$(-)$	$(+)$

Figure 19.15
An electrochemical cell involving the corrosion of iron.

Connecting wire

Fe — Cu

Aerated NaCl solution

Precipitate of Fe(OH)$_2$

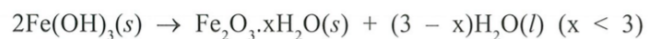| $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
Oxidation	Reduction
Anode	**Cathode**

Both ionic products will drift towards the other electrode, the Fe^{2+} towards the cathode and the OH$^-$ towards the anode. In between, they form a precipitate of green iron(II) hydroxide.

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$$
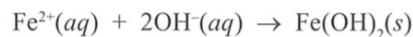
The iron(II) hydroxide will slowly oxidise further to brown iron(III) hydroxide by reaction with more dissolved oxygen in solution.

$$4Fe(OH)_2(s) + 2H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s)$$
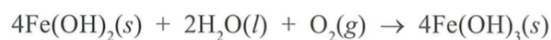
The iron(III) hydroxide may partially dehydrate to form rust.

$$2Fe(OH)_3(s) \rightarrow Fe_2O_3.xH_2O(s) + (3 - x)H_2O(l) \ (x < 3)$$

Although the formula of rust is variable it is often represented as Fe$_2$O$_3$.H$_2$O.

Rusting in the presence of other metals

The type of corrosion explained in the last section, which involves two different metals, is often referred to as 'galvanic action'. If two dissimilar metals are joined where dampness or wetting may occur an electrochemical or galvanic cell can be formed and the corrosion of the more reactive metal will be accelerated. The less reactive metal provides the cathodic surface for the reduction of atmospheric or dissolved oxygen. This commonly occurs in plumbing when copper water pipes are joined to galvanised iron pipes.

Figure 19.16
Where two dissimilar metals are joined the corrosion of the more reactive metal is accelerated.

Copper pipe (cathode)

Corrosion of iron

Iron pipe (anode)
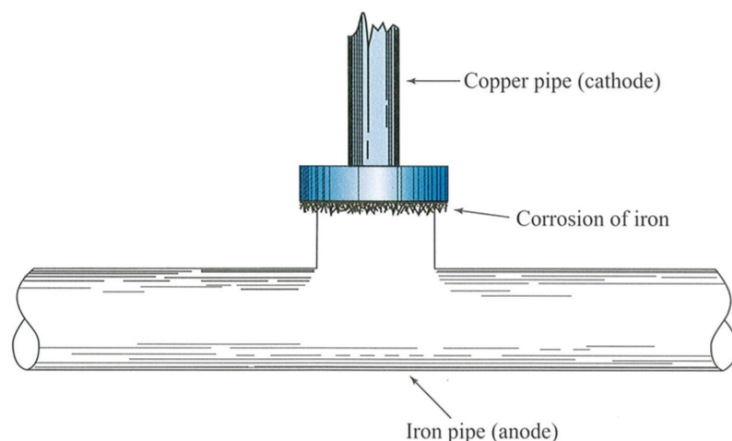
Caution should be exercised in using standard reduction potentials to predict galvanic corrosion. The electrolyte solution rarely contains the ions of the couples listed and concentrations are not likely to be 1 mol L^{-1}. Thus the reduction potentials may differ significantly from the standard values. Also, the presence of an oxide film on most metals inhibits their reactivity. For example, one would predict from Table 19.1 that aluminium would be the anode in a zinc/aluminium cell, but the aluminium is, in fact, the cathode. It behaves as a less reactive metal than zinc because of its fine tenacious oxide film.

Rusting in the absence of other metals

Besides corroding as part of a galvanic couple, iron will rust without contact with other metals. The surface oxide layer of an iron object formed by direct oxidation with air will have imperfections, such as fine cracks and thin sections.

When an electrolyte film covers the surface, anodic areas develop at these points because iron atoms migrate more easily through the oxide layer to become oxidised.
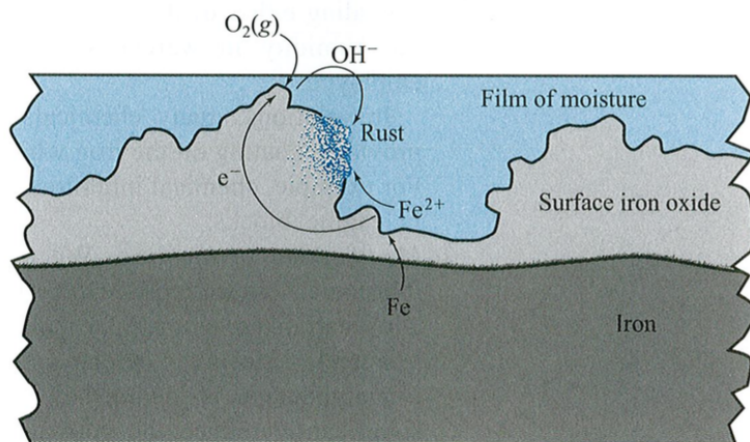
$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$
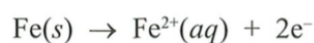
Oxygen is reduced to hydroxide ions at cathodic sites by electrons migrating from the anodic areas.

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

Iron(II) hydroxide forms and further oxidises to rust, as described previously. The overall equation can be written as follows.

$$4Fe(s) + 3O_2(g) + 2H_2O(l) \rightarrow 2Fe_2O_3.H_2O(s)$$

Figure 19.17
The surface corrosion of iron.

When iron undergoes oxidation, those parts of the iron surface which are most exposed to oxygen will become cathodic and hence be protected from corrosion (oxidation). Areas of limited oxygen contact will be anodic, and corrode. This phenomenon is called the 'differential aeration principle' and explains the rather unexpected observation that riveted steel plates will corrode in the crevices between the plates and not on the exposed surfaces. Similar observations can be made in metal joints and overlaps, particularly where debris accumulates and excludes oxygen.

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Figure 19.18
Crevice corrosion between riveted plates.
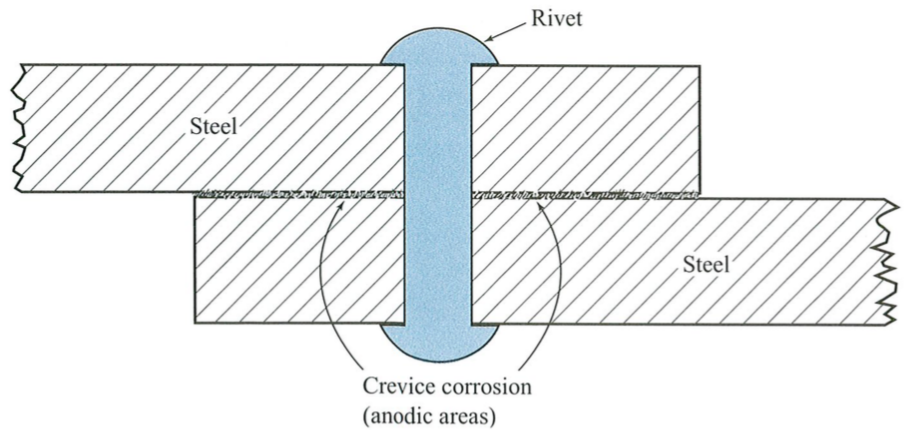
Prevention of rusting

From a consideration of the factors which influence the corrosion of iron, a large number of preventative measures can be deduced. Some of these are considered as follows.

1 *Modification of the environment*: As oxygen and moisture are essential to rusting, excluding either of these from contact with iron should be effective. Reducing the humidity in warehouses by refrigerated air-conditioning is sometimes employed.

   In solutions, many chemicals are used to absorb dissolved oxygen or to provide a coating on the iron which resists penetration by moisture and oxygen. For example, chemical inhibitors are added to radiator water to reduce corrosion in engine blocks.

2 *Modification of the iron*: When iron is alloyed with certain other elements it becomes less susceptible to corrosion. Steels containing chromium and having a low carbon content are particularly resistant, and are commonly used as 'stainless steels'. Steels can be made more resistant to corrosion under acid conditions if molybdenum is included in the alloy. Similarly, small amounts of copper significantly reduce the corrosion rate of mild steels.
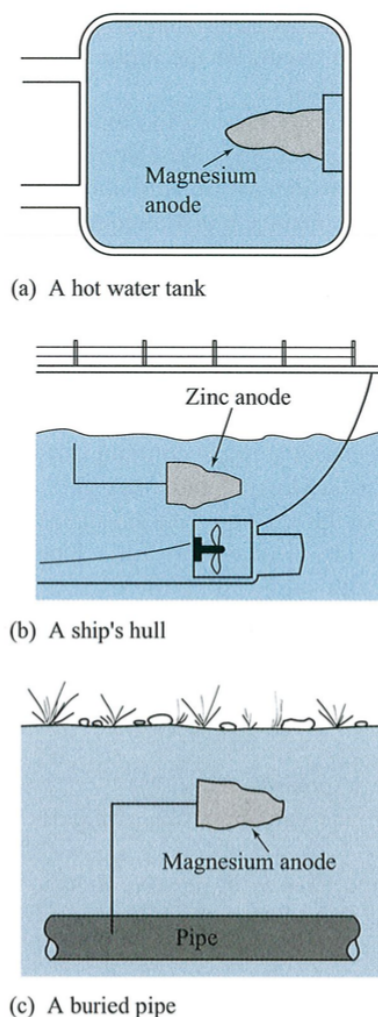
3 *Cathodic protection*: The corrosion of steel structures is often inhibited by making them cathodic. In fixed structures, such as jetties and pipelines, the steelwork is put at a negative potential by connecting it at intervals to a low-voltage D.C. source. The anodes may be old engine blocks or other pieces of scrap iron which gradually corrode away. More permanent anodes are now made of platinum-coated titanium rods. This method is used to protect wharves constructed in ocean environments.

Figure 19.19
The cathodic protection of a steel jetty. The jetty is kept at a negative potential using a low voltage D.C. source.
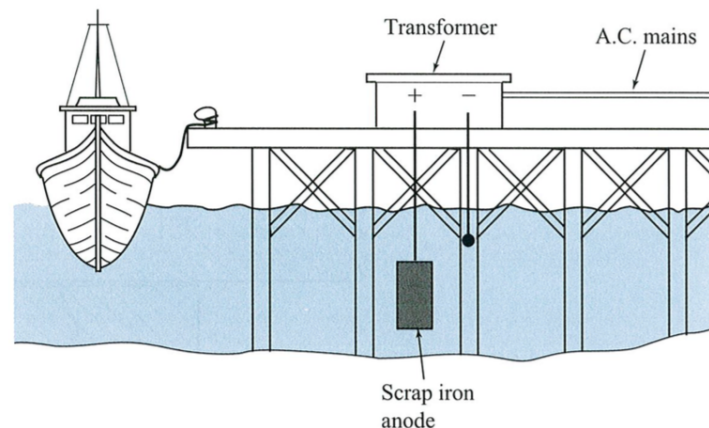
An alternative form of cathodic protection is to make the steel cathodic by connecting it electrically to a more active metal, such as zinc, aluminium or magnesium. The latter metal then corrodes away and is known as a 'sacrificial anode'. For this reason, zinc, aluminium and magnesium blocks are often attached to ships, boilers, pipelines and underground petrol tanks. A sacrificial magnesium anode in a hot water tank, for example, undergoes oxidation rather than the steel tank it is designed to protect.

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$$
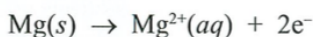
4 *Protective metallic coatings*: Many metals form their own protective oxide coating. When iron is covered with a layer of these metals the iron will also be protected from corrosion.

'Galvanised iron' is steel coated with zinc. The zinc reacts with oxygen and moisture in the air to form zinc hydroxide which absorbs carbon dioxide to form a basic zinc carbonate, $ZnCO_3.Zn(OH)_2$. This coating protects the zinc from further corrosion. A thin layer of zinc on mild steel therefore considerably lengthens the useful lifetime of the steel. As well as excluding water and oxygen, the zinc acts as a sacrificial anode if the zinc coating is broken. The zinc corrodes preferentially and thereby prolongs the life of the steel. Galvanised iron is commonly used for roofing, water tanks, water pipes and rubbish bins.

In 'tin plate', used in food and beverage cans, the tin coating excludes oxygen and water from the mild steel. If the tin coating is broken, however, the rate of corrosion of the steel is increased. The tin is less reactive than the steel and the latter is preferentially oxidised. However, the enhanced rate of rusting of discarded cans is environmentally favourable.

Chromium plating provides a protective and decorative finish on steel items such as car and bicycle parts, taps and jewellery. The steel is first nickel plated. The nickel protects the steel, but is itself susceptible to corrosion unless coated by chromium. Coatings of the less reactive metals copper, silver and gold must be absolutely free of gaps, otherwise the underlying steel will corrode rapidly.

5 *Protective non-metallic coatings*: Many other types of coatings are used to protect steel. Most provide an inert barrier to oxygen and moisture. They include oils, grease, paints, varnishes, enamels, glass and plastics. Care must be taken to ensure proper coverage. If paintwork is chipped or not fully adherent it is likely that rusting will occur rapidly in the partly covered areas, as explained by the differential aeration principle. For the same reason, a poorly applied coat of paint is probably more harmful than none at all, because rusting will start undetected under the surface of the painted areas.

Figure 19.20
The use of sacrificial anodes to protect iron and steel structures from corrosion.

(a) A hot water tank

(b) A ship's hull

(c) A buried pipe

The electrorefining of copper

Copper is principally extracted from sulfide ores such as chalcopyrite ($CuFeS_2$). A smelting process is employed to obtain crude copper of about 98% purity. In this process strong heating of the ore oxidises the sulfide to gaseous sulfur dioxide and reduces the copper to the metal.

$$2CuFeS_2(s) + 5O_2(g) + 2SiO_2(s) \rightarrow 2Cu(l) + 4SO_2(g) + 2FeSiO_3(l)$$
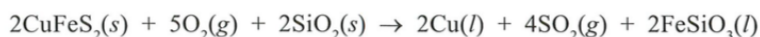
The silica removes iron as a slag.

The copper produced is called 'blister copper' because of the bubbly appearance produced by escaping sulfur dioxide. To obtain the 99.9% purity required for electrical wiring, the blister copper is refined electrolytically.

The impure copper is cast into slabs and made the anode of an electrolytic cell. The cathode is a thin sheet of pure copper and the electrolyte is copper(II) sulfate solution, acidified with sulfuric acid.

The copper and reactive metal impurities such as zinc, iron and nickel present in the anode are oxidised and enter the solution as ions. The sulfuric acid inhibits the evolution of oxygen gas at the anode from the oxidation of water. As the anode slab dissolves, the more inert metal impurities such as gold, silver and

Figure 20.3
The electrorefining of copper.

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

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$
Reduction
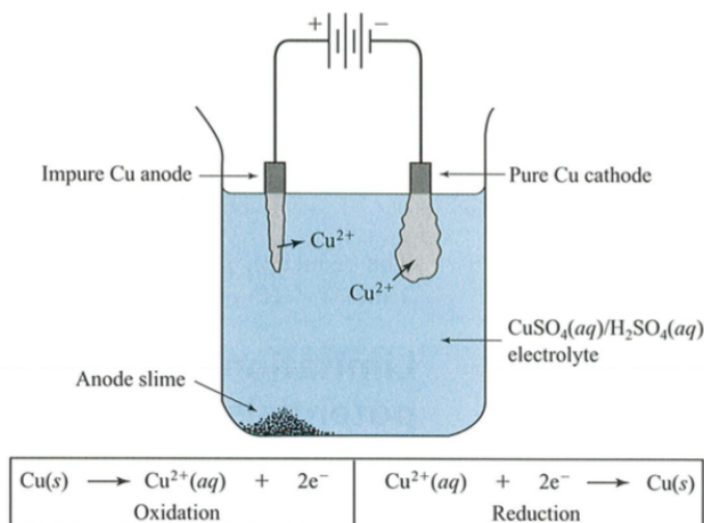
platinum fall to the bottom of the cell. In a finely divided state, they form an 'anode slime', which is a profitable source of these metals.

A small voltage is used so that pure copper deposits at the cathode. The ions of the more reactive metals remain in solution. These are removed periodically so that their concentrations do not build up sufficiently to cause them to be reduced. The copper that deposits at the cathode is extremely pure because almost all of the impurities present in the blister copper have been removed.

Copper is an important and widely used metal. Its properties and uses are summarised in Table 20.1.

Electroplating

Electroplating is used to add a thin layer of one metal onto another metal, either to improve its appearance or to increase its resistance to corrosion. Gold and silver plating are used to obtain the appearance of these metals but at a fraction of the cost. Steel is often electroplated to protect it from corrosion and to improve its appearance. For example, tin cans are made from mild steel plated with metallic tin, galvanised iron is coated with zinc, and chrome plated steel is often used in car bumper bars, wheel rims, bicycle handlebars, furniture and taps.

Electroplating processes are similar to electrorefining. The object to be plated is made the cathode of an electrolytic cell and the anode is the source of the plating metal. The anode dissolves by oxidation, yielding metal cations which are discharged as metal on the cathode. The electrolyte is an aqueous solution of a salt of the plating metal.

For example, in the electroplating of silver, the anode is a bar of silver and the electrolyte is a solution of a silver salt such as silver nitrate. The best electroplating is formed by small crystals which adhere strongly to the surface of the object. The conditions that favour the best quality electroplating are low concentrations of the relevant metallic cations and a small current. To maintain a low concentration of free silver ions in the electrolyte, they are complexed with cyanide ion according to the following equilibrium.
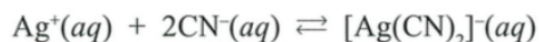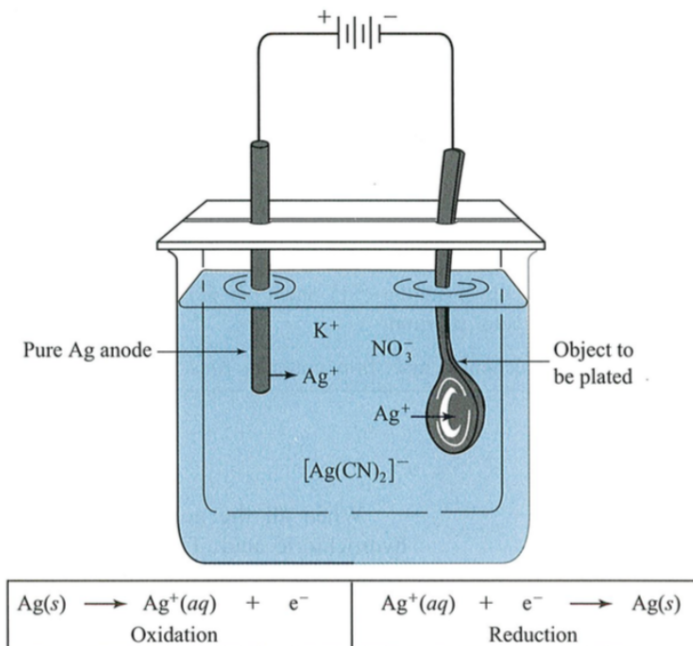
$$Ag^+(aq) + 2CN^-(aq) \rightleftharpoons [Ag(CN)_2]^-(aq)$$

Figure 20.5
In silver plating the object to be
plated is made the cathode of an
electrolytic cell.

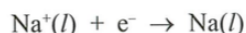| $Ag(s) \longrightarrow Ag^+(aq) + e^-$	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
Oxidation	Reduction

20.4
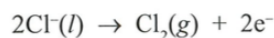# Electrolysis of sodium chloride

Molten sodium chloride

Sodium metal and chlorine gas are produced industrially in the Downs cell by the electrolysis of molten sodium chloride (Figure 20.7).
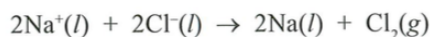
In the molten state the ions are free to move through the melt. Sodium metal is produced at the circular iron cathode.

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

Chlorine is evolved at the carbon anode.

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

The overall cell reaction is as follows.

$$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$$

The two products are kept separate by an iron screen between the electrodes, otherwise they would readily react and revert to sodium chloride. The molten sodium is less dense than the electrolyte and rises to the surface where it is tapped off. The chlorine is collected separately. The electrolyte of molten sodium chloride contains some added calcium chloride. This lowers the melting point of the sodium chloride from 801 °C to about 600 °C.
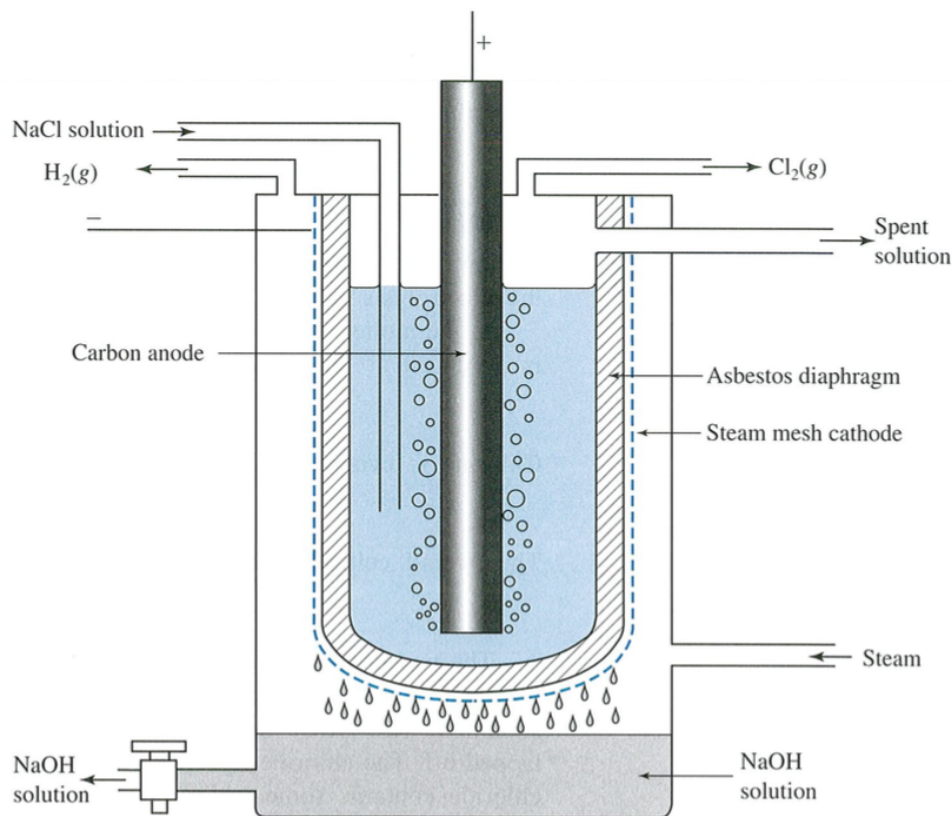
Figure 20.7
The Downs cell used in the electrolysis of molten sodium chloride.

Anode: $2Cl^-(l) \longrightarrow Cl_2(l) + 2e^-$

Cathode: $Na^+(l) + e^- \longrightarrow Na(l)$
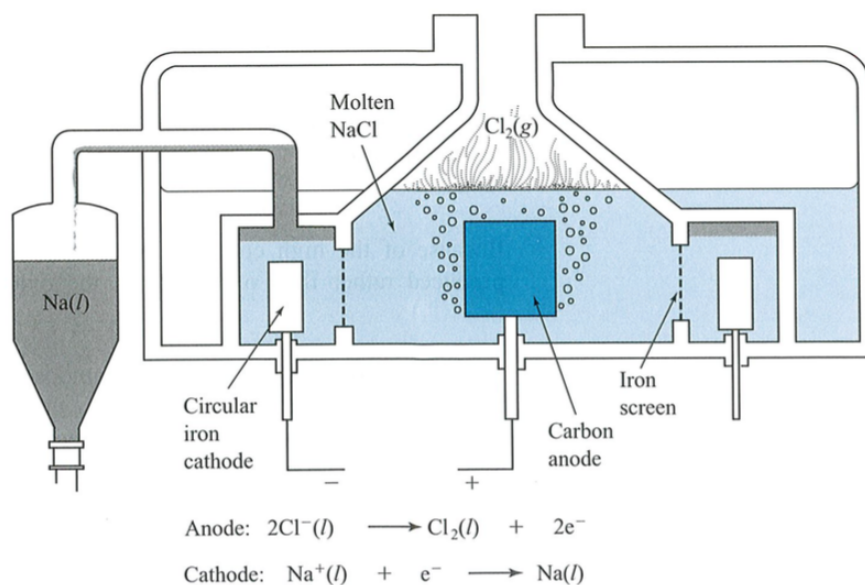
Aqueous sodium chloride

A concentrated aqueous solution of sodium chloride is electrolysed in the Nelson cell to produce sodium hydroxide, hydrogen and chlorine (Figure 20.8). The Nelson cell is also called a diaphragm cell because it contains an asbestos diaphragm which lines the steel-mesh cathode. The electrolyte solution soaks through the asbestos to the cathode and electrolysis takes place.
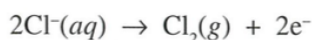
Anode: $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

Cathode: $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

At the steel cathode, water is reduced to hydrogen in preference to the reduction of sodium ions.

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$
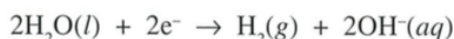
Because of the high concentration of chloride ions in the solution, chlorine is produced rather than oxygen from the oxidation of water.

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

Sodium ions move towards the cathode and with the hydroxide ions produced in the cathode reaction are washed to the bottom of the cell. This is achieved by passing steam over the cathode screen. The condensed steam washes out the ions and forms a hot solution of sodium hydroxide at the bottom of the cell. Solid sodium hydroxide can be crystallised out from this solution.

The overall cell reaction is given by the following equation.

$$2Na^+(aq) + 2Cl^-(aq) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g) + Cl_2(g)$$

In this process three important substances, hydrogen, chlorine and sodium hydroxide, are manufactured from the electrolysis of an aqueous solution of the relatively cheap raw material, sodium chloride. All of the products have numerous industrial uses. Hydrogen is used in the manufacture of ammonia, chlorine in water treatment and the manufacture of hydrochloric acid and PVC, and sodium hydroxide in the extraction of aluminium.

Fuel cells

Fuel cells differ from primary and secondary electrochemical cells in several ways. The major distinction is that fuel cells store neither the reactants nor the products. Their action is to supply electricity at a constant rate as reactants are fed into them and products are removed. They are direct energy converters. Another feature of fuel cells is that the reactants are usually gaseous, rather than being the solid substances commonly used in primary and secondary cells.

The most successful fuel cell so far developed has been that based on the combination of hydrogen and oxygen. The net reaction is the same as that for the combustion of hydrogen.

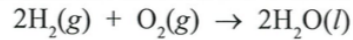$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Figure 19.10 shows one form of hydrogen–oxygen fuel cell.

Hydrogen gas is supplied to the anode chamber and oxygen to the cathode chamber. The gases diffuse through the electrodes which are porous metals such as platinum or nickel, and act as catalysts. The gases react with the electrolyte which may be acidic or alkaline. For an acidic electrolyte, the reactions are given by the following equations.
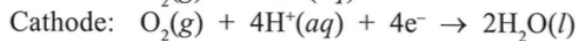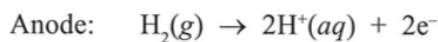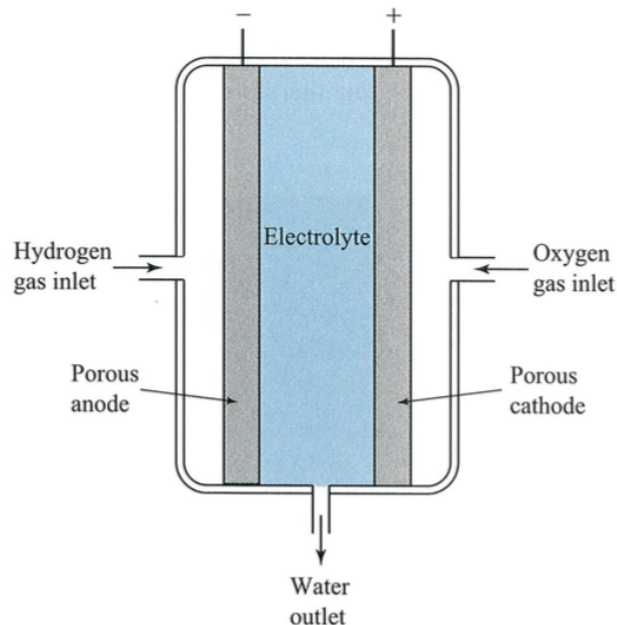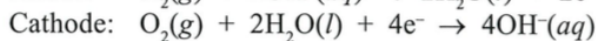
Anode: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$
Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Figure 19.10
A hydrogen–oxygen fuel cell.

If the electrolyte is alkaline, the reactions are as follows.

Anode: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$
Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

In both types of fuel cell the overall equation is the same.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$
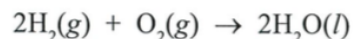
The theoretical e.m.f. of 1.23 V is difficult to attain. One of the major problems is associated with the electrolyte. As the electrode reactions occur, the H^+ ions in the acidic electrolyte must migrate from the anode to the cathode. In the alkaline

electrolyte, OH⁻ ions must move from the cathode to the anode. At normal temperatures, the rate at which these ions move is a limiting factor.

Another problem concerns the electrodes. These must provide intimate contact between the gaseous reactants, the electrolyte and the catalyst. One development is to use graphite electrodes with large pores on the gas side and fine pores on the liquid electrolyte side. The finely divided metal catalyst adheres to the inside surface of the pores. Surface tension causes the liquid electrolyte to be retained in the finer pores while the gases diffuse into them from the larger pores.

Fuel cells are part of a developing technology. Major advantages of fuel cells are their relatively small mass and high fuel efficiency. Spacecraft including the Apollo and space shuttle programs have been using fuel cells for many years as a source of electrical energy and water. In spacecraft, the hydrogen and oxygen are stored as liquids until needed.

Figure 19.11
A PC17 Space Shuttle fuel cell power plant, rated at 12 kilowatts. (*International Fuel Cells, Connecticut, USA.*)