

CHAPTER 09

Galvanic cells

By the end of this chapter, you will know how galvanic cells generate electricity from chemical reactions. You will see how experimental data from galvanic cells can be used to compare the relative strengths of oxidising and reducing agents.

The relative strengths of oxidising and reducing agents are conveniently summarised in a table known as the electrochemical series. You can use the electrochemical series to predict the likelihood of individual redox reactions occurring, and to calculate the potential differences of different galvanic cells.

Finally, you will investigate how different types of galvanic cells are used as a source of power for a range of uses.

Science as a human endeavour

- Spontaneous redox reactions can be used as a source of electrical energy, including primary, secondary and fuel cells. Fuel cells are a potential lower-emission alternative to the internal combustion engine and are already being used to power various modes of transport. Organisations, including the International Partnership for Hydrogen and Fuel Cells in the Economy, have been created to foster global cooperation on research and development, common codes and standards, and information sharing on infrastructure development.

Science understanding

- electrochemical cells, including galvanic and electrolytic cells, consist of oxidation and reduction
- half-reactions connected via an external circuit through which electrons move from the anode (oxidation reaction) to the cathode (reduction reaction)
- galvanic cells produce an electric current from a spontaneous redox reaction
- electrochemical cells can be described in terms of the reactions occurring at the anode and cathode, the role of the electrolyte, salt bridge (galvanic cell), ion migration, and electron flow in the external circuit
- cell diagrams can be used to represent electrochemical cells
- the relative strength of oxidising and reducing agents can be determined by comparing standard electrode potentials, and can be used to predict reaction tendency
- the electric potential difference of a cell under standard conditions can be calculated from standard electrode potentials; these values can be used to compare the voltages generated by cells constructed from different materials
- a range of reactions involve the oxidation of one species and reduction of another species, including metal and halogen displacement reactions, combustion and corrosion

9.1 Galvanic cells



FIGURE 9.1.1 Your way of life depends on cells and batteries.

Electronic devices such as mobile phones, notebook computers, cameras and hearing aids all depend on small portable sources of electricity: cells and batteries (Figure 9.1.1). Portable energy in the form of cells and batteries enables you to operate electrical equipment without the restrictions of a power cord.

The demand for electronic devices has stimulated the production of a variety of cells, from tiny button cells for watches and calculators, to the huge batteries used to operate lighthouses. The energy provided by cells and batteries may be more expensive than energy from other sources, such as fossil fuels, but this cost is offset by their convenience.

In this section, you will find out how cells are constructed, and how they provide you with a source of electrical energy.

CHEMISTRY IN ACTION

A technological leap beginning with a frog's leg

The history of electrochemistry began in 1791 when Italian biologist Luigi Galvani and his assistant were experimenting with dissected frogs. They hung a frog's leg on a copper hook and were startled to see the leg twitch when it touched an iron rail. The muscles of the frog were stimulated by an electric shock. Galvani had just discovered how to generate a current. His 'error' was in thinking that the current was some sort of life force, a perfectly reasonable idea for the time.

Other scientists set out to investigate the possibility that metals were involved in this phenomenon. After several years' work, in 1800, Alessandro Volta developed a device that used a chemical reaction to produce an electric current. Figure 9.1.2 shows the device, now called a 'voltaic pile'. It consisted of a stack of alternating copper and zinc discs separated by cardboard soaked in salt water.



FIGURE 9.1.2 An original voltaic pile. The pile is 15 cm high and contains alternating copper and zinc discs separated by cardboard.

INTRODUCING GALVANIC CELLS

An **electrochemical cell** is a device in which chemical energy is converted into electrical energy, or vice versa. A **galvanic cell** (also known as a **voltaic cell**) is a type of electrochemical cell in which chemical energy is converted into electrical energy. The cells in your mobile phone and laptop are galvanic cells.

If you connect several cells in series to obtain a higher potential difference or 'voltage', the combination of cells is called a **battery**. The term 'battery' strictly only applies to a combination of cells, but it is in everyday use to describe cells as well.

Figure 9.1.3 shows how you can produce a galvanic cell from simple laboratory equipment.



FIGURE 9.1.3 Construction of a galvanic cell from simple laboratory equipment.

In Figure 9.1.4, you can see a diagram of a Daniell cell, named after the scientist who invented it in 1836, John Daniell. The Daniell cell produces an electric current that flows through the wire and light globe. This part of the cell is called the **external circuit**. The globe converts the electrical energy of the current into light and heat.

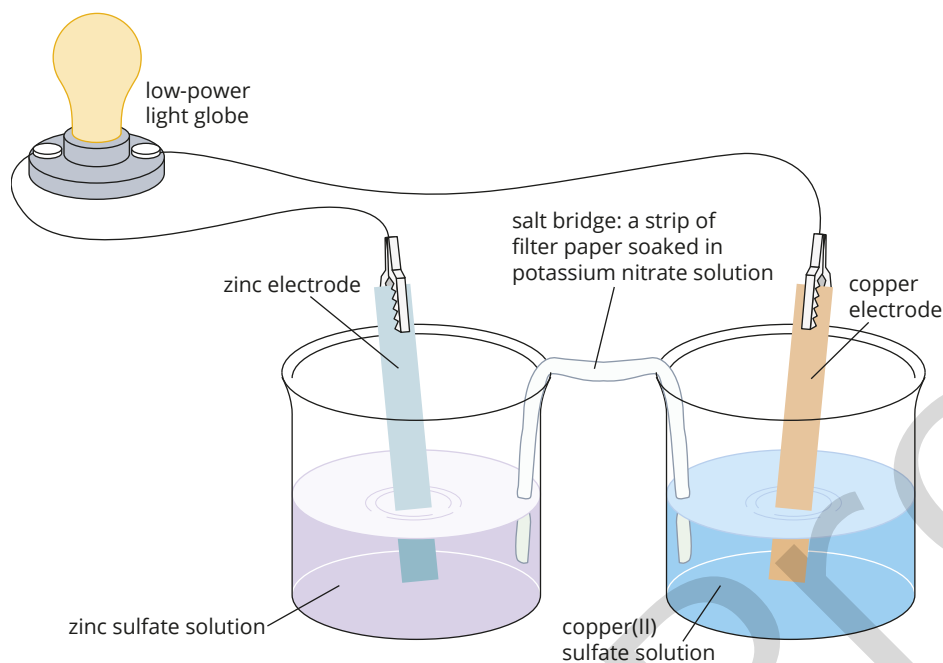


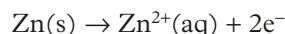
FIGURE 9.1.4 The Daniell cell is a type of galvanic cell.

The current flows because a chemical reaction is taking place in the cell. If you leave the cell with a light globe connected for several hours, you will see evidence of this reaction occurring: the zinc metal corrodes, the copper metal becomes covered with a furry dark brown deposit and the blue copper(II) sulfate solution loses some of its colour.

If you replace the light globe with a **galvanometer** (an instrument for detecting electric current), the galvanometer will indicate that electrons flow from the zinc **electrode** through the wire to the copper electrode. Current flows only if the two halves of the cell are connected by a **salt bridge**. A salt bridge is often made from filter paper soaked in a relatively unreactive **electrolyte**, such as a solution of potassium nitrate.

These observations lead to the following explanations about what is occurring in a galvanic cell.

- The reaction in the cell is a **redox reaction**, because electrons are being transferred.
- The zinc electrode corrodes because the zinc metal forms zinc ions in solution:



- The oxidation of the zinc metal releases electrons, which flow through the wire to the copper electrode.
- Electrons are accepted by copper(II) ions in the solution when the ions collide with the copper electrode:



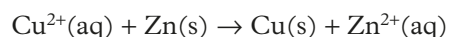
- The copper metal that is formed deposits on the electrode as a dark brown coating.

CHEMFILE

The Daniell cell

In 1836, English chemist John Daniell invented a device that could supply a useful electric current. The device, which became known as the Daniell cell, was used almost exclusively to power the early English and US telegraph systems because of its reliable output.

In this cell, chemical energy is transformed into electrical energy. Figure 9.1.5 shows the processes that occur during the operation of the cell. The equation for the overall reaction is found by adding the two half-equations:



Note that when these half-equations are added together, there would be the same number of electrons (two) on each side of the equation so they are cancelled out and don't appear in the final equation.

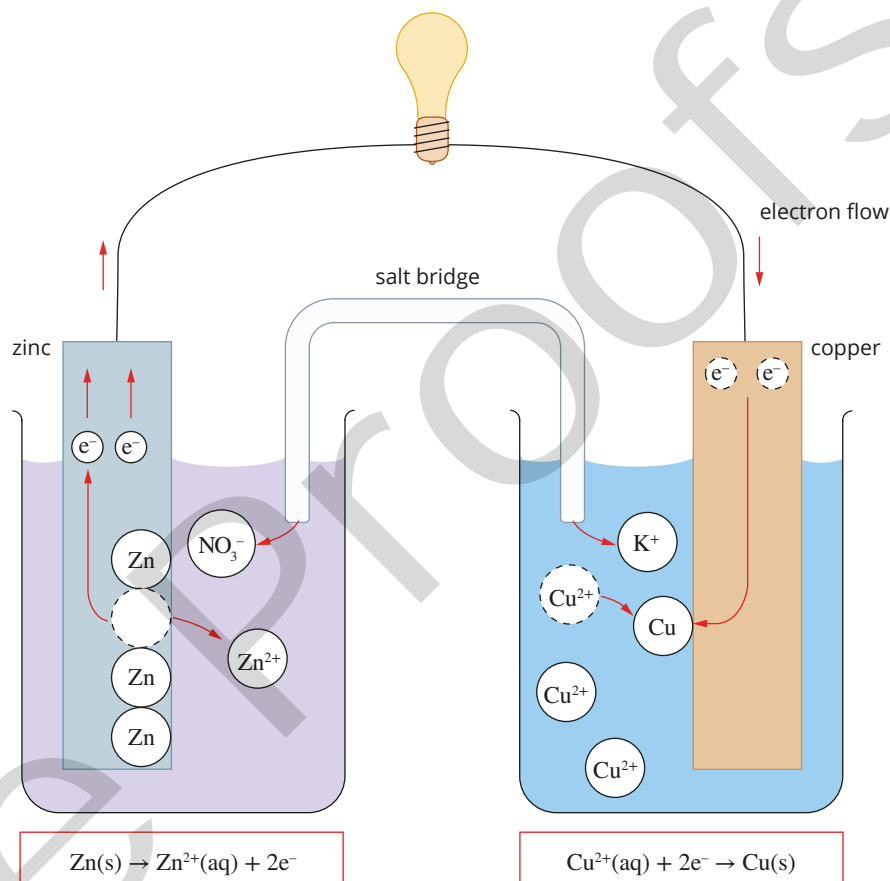


FIGURE 9.1.5 A representation of the electrode reactions in a Daniell cell. The salt bridge contains potassium nitrate solution.



FIGURE 9.1.6 $\text{Cu}^{2+}(\text{aq})$ ions in blue-coloured copper(II) sulfate solution reacting directly with a strip of zinc metal

This redox reaction is described as a **spontaneous reaction** because it occurs naturally.

Copper(II) ions act as the **oxidising agent**, or **oxidant**, and zinc metal acts as the **reducing agent**, or **reductant**.

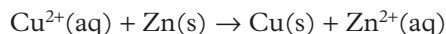
i A chemical that causes another substance to be oxidised is called an oxidising agent and is itself reduced in the redox reaction. Similarly, a chemical that causes another substance to be reduced is called a reducing agent. Reducing agents are oxidised in redox reactions.

ENERGY TRANSFORMATIONS IN DIRECT REACTIONS

You may have seen a similar reaction to the one that occurs in a Daniell cell if you have copper-plated a piece of metal, such as zinc. When zinc is immersed in an aqueous solution containing $\text{Cu}^{2+}(\text{aq})$ ions, the metal becomes coated in dark brown copper (Figure 9.1.6).

At the same time, thermal energy is produced, which escapes into the surrounding environment as heat.

The overall equation for this metal displacement reaction is:



This reaction is an example of a spontaneous exothermic reaction. If the reactants are allowed to come into direct contact with each other, their chemical energy is transformed directly to thermal energy. However, in a galvanic cell, the half-reactions occur in separate containers, and the electrons are transferred through the external circuit so that chemical energy is transformed into electrical energy.

The energy changes that occur in galvanic cells and when reactants undergo direct reaction are summarised in Figure 9.1.7.

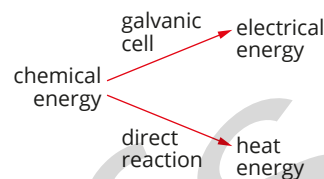


FIGURE 9.1.7 Energy transformations that occur when reactants are separated in a galvanic cell and when the reactants react directly

HOW A GALVANIC CELL OPERATES

A galvanic cell is designed so that half-reactions occur in two separate compartments of the cell. Because the oxidising agent and reducing agent do not come into direct contact with each other, electrons can only be transferred through an external circuit connecting the negative and positive electrodes.

This flow of electrons creates an electric current. Therefore, the chemical energy of the reactants is transformed into electrical energy.

Half-cells

A galvanic cell can be regarded as consisting of two **half-cells**. Each half-cell contains an electrode in contact with a solution (Figure 9.1.8). In the Daniell cell, one half-cell contains $\text{Cu}(\text{s})$ and $\text{Cu}^{2+}(\text{aq})$; the other contains $\text{Zn}(\text{s})$ and $\text{Zn}^{2+}(\text{aq})$. The species present in each half-cell forms a **conjugate redox pair** (an oxidising agent and its corresponding reduced form).

If one member of the conjugate pair in a half-cell is a metal, it is usually used as the electrode. Some redox pairs, such as $\text{Br}_2(\text{aq})/\text{Br}^-(\text{aq})$ and $\text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq})$, do not involve solid metals. If no metal is present, an **inert** (unreactive) **electrode**, such as platinum or graphite, is used, as shown in Figure 9.1.8.

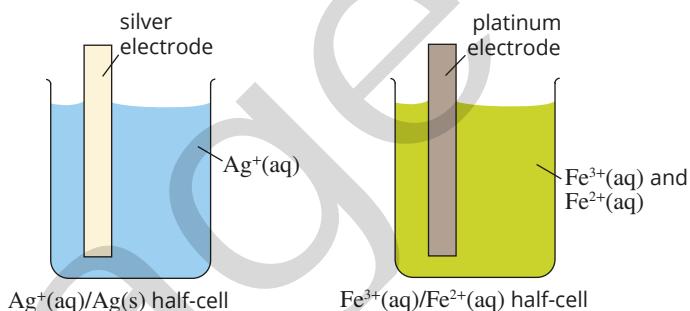


FIGURE 9.1.8 Typical half-cells. The $\text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq})$ half-cell on the right does not contain a solid metal to act as an electrode, so an inert platinum electrode has to be added.

In some half-cells, one of the conjugate pairs may be a gas. In such cases, the special ‘gas electrode’ like the one shown in Figure 9.1.9 for the $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ half-cell is used. Note that half-cells usually contain other species not involved in the reaction, such as spectator ions and the solvent.

The electrode at which oxidation occurs is called the **anode**. In a galvanic cell, the anode, where electrons are released, is described as the negative terminal. The electrode at which reduction occurs is called the **cathode**. The cathode, where electrons are gained, is the positive terminal in a galvanic cell.

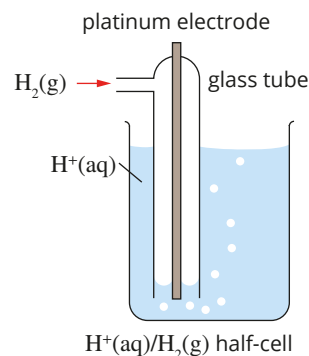


FIGURE 9.1.9 A $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ half-cell consists of a platinum rod in a solution of $\text{H}^+(\text{aq})$ with H_2 gas bubbling through the solution.

Purpose of the salt bridge

The salt bridge contains ions that are free to move so that they can balance charges formed in the two compartments. *Cations* move towards the *cathode* and *anions* move towards the *anode*.

i Cations in the salt bridge move towards the cathode and anions in the salt bridge move towards the anode.

Without a salt bridge, as the reaction proceeded, the solution in one compartment in the galvanic cell would accumulate negative charge and the solution in the other compartment would accumulate positive charge. Such accumulation of charge would stop the reaction very quickly and, hence, prevent further reaction.

The salt bridge is also called the **internal circuit**.

WRITING HALF-CELL EQUATIONS

If a conjugate redox pair consists of an element and its corresponding ion, then the half-equation is relatively easy to write. For instance, knowing that a reduction reaction involves the conjugate redox pair of Zn^{2+} ions and Zn, you can simply write the half-cell equation as:



Half-cell equations involving polyatomic ions may be more complex to write. The equation for the reduction reaction in a half-cell containing the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) and Cr^{3+} ion redox pair is:



You learnt to write half-equations such as these in Chapter 8.

Writing an overall equation for a cell reaction

The half-equations for the oxidation and reduction reactions that occur in a cell can be added together to obtain an overall, or full, equation. An overall equation does not show any electrons; all the electrons lost in the oxidation reaction are gained in the reduction reaction. You may need to multiply one or both half-equations by a factor to ensure that the electrons balance and can be cancelled out in the overall equation.

DRAWING AND LABELLING A DIAGRAM OF A GALVANIC CELL

If you know the reaction occurring in a galvanic cell, then you can draw a diagram of the cell. The diagram will identify key features, such as the anode, cathode, electrode polarity, direction of electron flow in the external circuit and direction of the flow of ions in the solutions and the salt bridge.

For example, consider a cell with the cell reaction:



From this reaction, you can see that:

- copper metal is at the anode (because copper is oxidised and oxidation occurs at the anode)
- chlorine gas is present at the cathode (because chlorine is reduced and reduction occurs at the cathode).

i In balanced half-equations and overall equations, the:

- number of atoms of each element is equal on both sides
- total charge on each side is equal.

i The number of electrons lost in the oxidation reaction must equal the number of electrons gained in the reduction reaction.

As in all galvanic cells:

- electrons flow through the external circuit from the anode (negative) to the cathode (positive)
- anions flow in the internal circuit to the anode and cations flow towards the cathode.

This information is used to draw and label the diagram of the cell as shown in Figure 9.1.10.

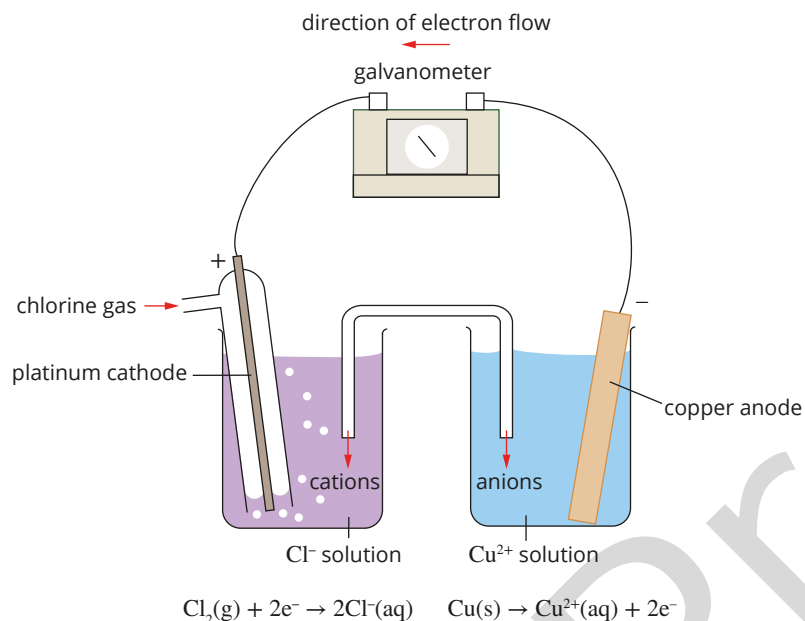


FIGURE 9.1.10 A diagram of the cell containing $\text{Cl}_2(\text{g})/\text{Cl}^-(\text{aq})$ and $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ half-cells

Shorthand cell notation

A useful shorthand notation can be used to describe the components of a galvanic cell. For example, the Daniell cell shown earlier (Figure 9.1.4) can be represented as shown in Figure 9.1.11.

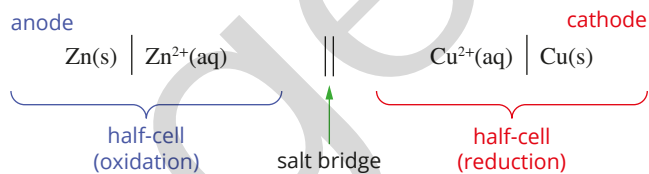
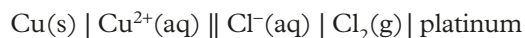


FIGURE 9.1.11 A shorthand representation of the Daniell cell, which contains $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$ and $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ half-cells

The components of the half-cell that contains the anode, and undergoes oxidation, are shown on the left. The components of the half-cell that contains the cathode, and undergoes reduction, are shown on the right. A double vertical line represents the salt bridge and single vertical lines are used to separate chemicals in different physical states.

The cell shown in Figure 9.1.10 is represented as:



Note that the electrode that is negatively charged is on the far left and the electrode that is positively charged is on the far right.

9.1 Review

SUMMARY

- The reactions that occur in galvanic cells are spontaneous and exothermic.
- In a galvanic cell, chemical energy is converted directly into electrical energy in a redox reaction.
- A cell is made from two half-cells.
- Each half-cell contains a conjugate redox pair.
- An oxidation reaction occurs in one half-cell and a reduction reaction occurs in the other half-cell.
- The electrode in the half-cell in which oxidation occurs is called the anode; the electrode in the half-cell in which reduction occurs is called the cathode.
- In galvanic cells, the anode is negative and the cathode is positive.
- Electrons flow through the external circuit from the anode to the cathode.
- A salt bridge allows a cell to produce electricity by preventing the accumulation of charge. Cations in the salt bridge move towards the cathode and anions move towards the anode.
- If the reactants in a galvanic cell reaction are allowed to come into direct contact, chemical energy is converted into heat energy rather than electrical energy.

- Galvanic cells can be represented by cell diagrams and by a shorthand notation.
- Key concepts about a galvanic cell are summarised in Figure 9.1.12.

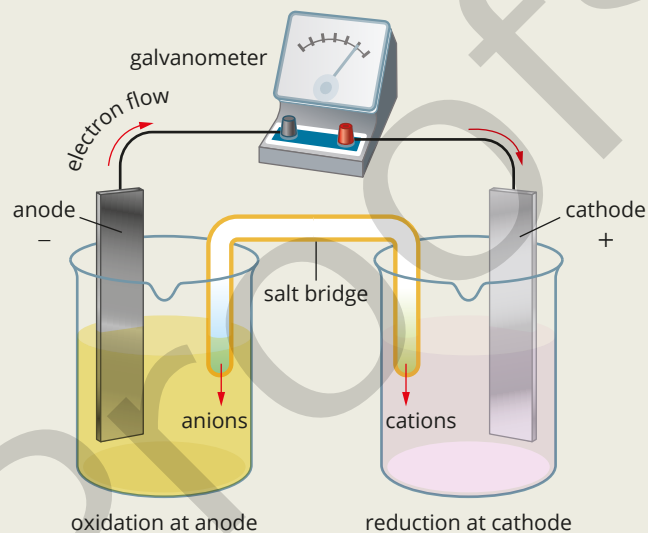


FIGURE 9.1.12 Key concepts about how a galvanic cell works.

KEY QUESTIONS

- 1 Which one of the following statements about a galvanic cell is correct?
 - A The electrode where oxidation occurs is the cathode.
 - B Electrons flow towards the electrode where oxidation occurs.
 - C Anions flow into the half-cell containing the electrode where reduction occurs.
 - D The electrode where oxidation occurs has a negative polarity.
- 2 Draw labelled diagrams of the following half-cells.
 - a $\text{Ni}^{2+}(\text{aq})/\text{Ni}(\text{s})$
 - b $\text{Sn}^{4+}(\text{aq})/\text{Sn}^{2+}(\text{aq})$
 - c $\text{H}^{+}(\text{aq})/\text{H}_2(\text{g})$
- 3 The overall equation for the reaction that occurs in a cell made up of $\text{Al}^{3+}(\text{aq})/\text{Al}(\text{s})$ and $\text{Sn}^{2+}(\text{aq})/\text{Sn}(\text{s})$ half-cells is:
$$2\text{Al}(\text{s}) + 3\text{Sn}^{2+}(\text{aq}) \rightarrow 2\text{Al}^{3+}(\text{aq}) + 3\text{Sn}(\text{s})$$
Write half-equations for the reaction occurring at the:
 - a cathode
 - b anode.
- 4 Draw a diagram of the cell from Question 3 and label the:
 - half-equation for the reaction occurring in each half-cell
 - anode and cathode
 - direction of electron flow
 - electrode polarities (which electrode is positive and which is negative)
 - direction of anion and cation flow from the salt bridge.

- 5 Write the cell from Question 3 using shorthand cell notation.
- 6 In the spaces provided, label the galvanic cell in Figure 9.1.13 with:
- anode
 - cathode
 - positive electrode
 - negative electrode
 - reduction
 - oxidation
 - salt bridge.

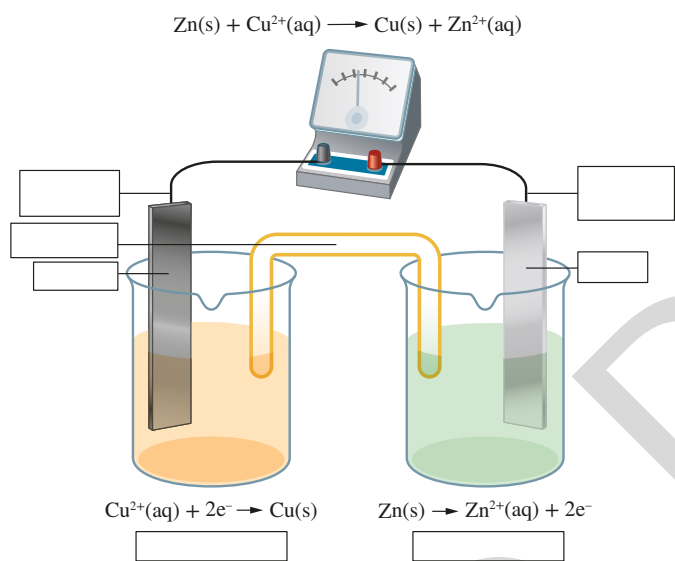


FIGURE 9.1.13 A galvanic cell

9.2 The electrochemical series



FIGURE 9.2.1 Sodium is highly reactive. When water is dropped onto sodium metal, the products are sodium hydroxide and hydrogen gas.

As you saw in Chapter 8, metals vary in their reactivity. Platinum and gold are unreactive and widely used for jewellery. Other metals are very reactive. For example, sodium reacts so readily with oxygen and water (Figure 9.2.1) that it must be stored in paraffin oil.

Galvanic cells can help you compare the relative reactivity of metals. Galvanic cells can be constructed from various combinations of half-cells. The experimental data collected from these combinations allows chemists to determine the oxidising and reducing strengths of many different substances. This information is very useful because it allows you to predict the products of various reactions, calculate the voltages of cells and develop more powerful and longer-lasting batteries.

RELATIVE OXIDISING AND REDUCING STRENGTHS

A half-cell contains a conjugate redox pair. The reactions that can occur in a half-cell can be written as reversible reactions, showing the relationship between the two chemicals in the redox pair. For example, the reaction in a:

- half-cell containing the $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ redox pair may be written as:



- half-cell containing the $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$ redox pair may be written as:



Figure 9.2.2 shows a diagram of a cell constructed from $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ and $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$ half-cells.

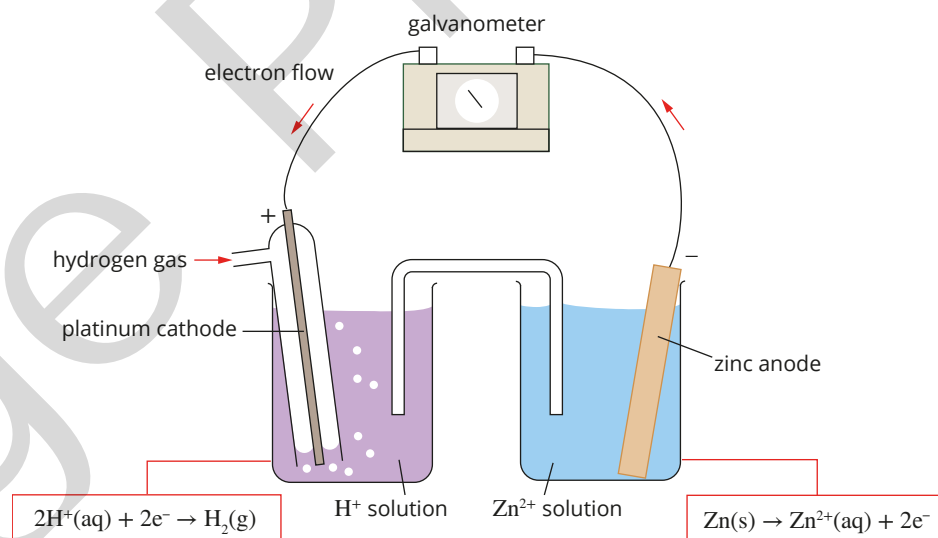
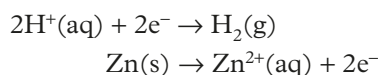


FIGURE 9.2.2 A diagram of a cell constructed from $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ and $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$ half-cells

Notice that in this cell, the zinc electrode is negative. The reactions that are occurring are:



Zn is oxidised to Zn^{2+} , and H^+ is reduced to H_2 . Zinc can be described as a reducing agent or reductant because it causes the reduction of H^+ . The H^+ is described as an oxidising agent or oxidant because it causes the Zn to be oxidised to Zn^{2+} .

Because electrons flow from the Zn^{2+}/Zn half-cell to the H^+/H_2 half-cell, you can infer that:

- zinc is a stronger reducing agent than H_2
- H^+ is a stronger oxidising agent than Zn^{2+} ions.

i In a galvanic cell, the stronger reducing agent is in the half-cell with the negative electrode (anode). The stronger oxidising agent is in the half-cell with the positive electrode (cathode).

POTENTIAL DIFFERENCE

A current flows in a galvanic cell because one half-cell has a greater tendency to push electrons into the external circuit than the other half-cell. Chemists say that a **potential difference** exists between the two half-cells. The potential difference of a cell is sometimes also called the **electromotive force**, or emf, and is commonly referred to as the voltage.

The potential difference of a cell, symbol E , has the unit of a **volt** (V) and is measured with a **voltmeter**.

Potential differences of cells are usually measured under the **standard conditions** of:

- a pressure of 1 bar (100 kPa)
- 1 mol L⁻¹ concentration of solutions.

The potential difference of a cell under standard conditions is given the symbol E° . Potential differences are usually measured at 25°C.

Standard electrode potentials

It is impossible to measure the potential difference of an isolated half-cell because both oxidation and reduction must take place for a potential difference to exist. However, you can assign a standard half-cell potential (E°) to each half-cell by connecting the cells to a standard reference half-cell and measuring the voltage produced.

A hydrogen half-cell, H⁺(aq)/H₂(g), under standard conditions, is used for this purpose and its E° value is arbitrarily assigned as zero. This half-cell is known as the **standard hydrogen half-cell** or standard hydrogen electrode.

The **standard electrode potential** of other cells may then be measured by connecting them to the standard hydrogen half-cell, as shown in Figure 9.2.4 for the Fe²⁺(aq)/Fe(s) half-cell.

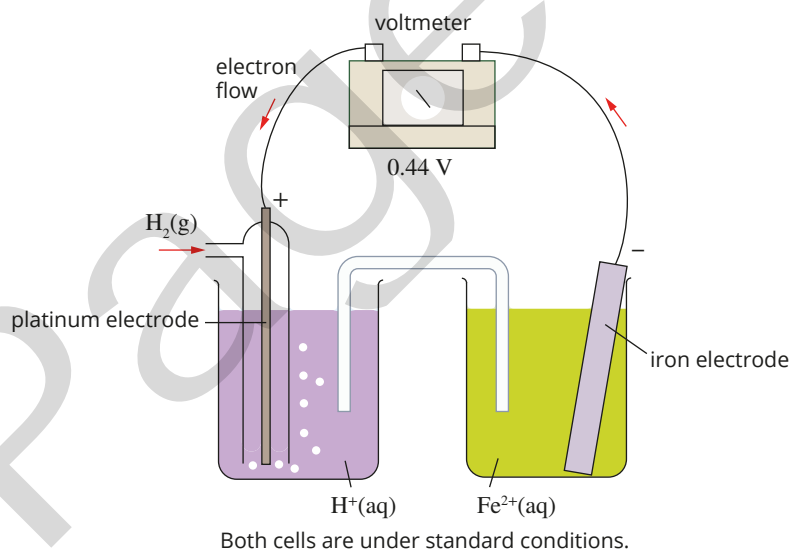


FIGURE 9.2.4 Measuring the standard half-cell potential of a Fe²⁺(aq)/Fe(s) half-cell. From the voltmeter reading and negative polarity of the iron electrode, the E° of this half-cell is -0.44 V.

The information obtained from this measurement shown in Figure 9.2.4 can be summarised as follows:



CHEMFILE

Electrical energy from a lemon

You can generate electrical energy from a lemon or other fruit. As well as the lemon, you need a galvanised iron nail, a copper nail and two wires with crocodile clips at each end.

To make a galvanic cell, squeeze the lemon, without breaking its skin, to release its juices. Then push both nails half their length into the lemon, with the nails about 5 cm apart. Connect the nails to separate wires.

The free ends of the wires of this cell can then be connected to low current electronic devices, such as a battery-operated digital clock, an LED light or cheap calculator (Figure 9.2.3). A stronger source of electricity can be created by making several of these lemon cells and using wires to connect them in series to make a battery. (Use a wire to connect the zinc metal in one lemon directly to the copper metal in another lemon.)



FIGURE 9.2.3 An electrical cell made from a lemon

The zinc metal on the surface of the iron nail is oxidised to Zn²⁺ and H⁺ in the acidic lemon juice is reduced to H₂. The cell is similar to the one shown earlier in Figure 9.2.2.

The negative sign indicates that the electrode in the half-cell was negative when connected to the hydrogen half-cell. Oxidation is occurring in the $\text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s})$ half-cell and the electrons that are produced from the iron electrode move towards the hydrogen half-cell. The value of -0.44 V is known as both the standard electrode potential and the **standard reduction potential**. The standard electrode potential gives a numerical measure of the tendency of a half-cell reaction to occur as a reduction reaction.

THE ELECTROCHEMICAL SERIES

By connecting the standard hydrogen electrode to different half-cells and measuring their standard reduction potentials, chemists have developed a table called the **electrochemical series** (Figure 9.2.5).

Half-reaction	E° (volts)
$\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-(\text{aq})$	+2.89
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.76
$\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	+1.69
$2\text{HClO}(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	+1.63
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.51
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Au}(\text{s})$	+1.50
$\text{HClO}(\text{aq}) + \text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+1.49
$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+1.46
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+1.36
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.36
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	+1.08
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2(\text{aq})$	+0.70
$\text{I}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$	+0.54
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightleftharpoons 4\text{OH}^-(\text{aq})$	+0.40
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34
$\text{S}(\text{s}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{S}(\text{aq})$	+0.17
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0 exactly
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{s})$	-0.24
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Co}(\text{s})$	-0.28
$\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.36
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cd}(\text{s})$	-0.40
$2\text{CO}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4(\text{aq})$	-0.43
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Cr}(\text{s})$	-0.74
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Mn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Al}(\text{s})$	-1.68
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg}(\text{s})$	-2.36
$\text{Na}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ca}(\text{s})$	-2.87
$\text{Sr}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Sr}(\text{s})$	-2.90
$\text{Ba}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ba}(\text{s})$	-2.91
$\text{K}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{K}(\text{s})$	-2.94

FIGURE 9.2.5 The electrochemical series. The strongest oxidising agents are at the top left of the table and the strongest reducing agents are at the bottom right of the table.

Under non-standard conditions, the order of the half-cells may change.

Notice the value of 0.00 V given for the $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ half-equation. All other E° values are relative to this arbitrary standard. The strongest oxidising agent, F_2 , is at the top left of the table and the strongest reducing agent, Li , is at the bottom right of the table.

In a galvanic cell, the stronger reducing agent is oxidised, so it is in the half-cell with the negative electrode (anode). The stronger oxidising agent is reduced, so it is in the half-cell with the positive electrode (cathode).

USING THE ELECTROCHEMICAL SERIES

Predicting cell reactions

You can use the electrochemical series to predict what will happen when two specific half-cells are combined to form a cell. The strongest oxidising agent in the cell will react with the strongest reducing agent.

Another way to predict the electrode reactions is to remember that the half-reaction that is higher in the electrochemical series goes forward and the lower one is reversed. (This is sometimes called the 'clockwise rule'.) As a consequence:

- a reduction reaction will occur in the half-cell with the higher E° value, whereas an oxidation reaction will occur in the half-cell with the lower E° value
- the positive electrode will be in the half-cell with the higher E° value, whereas the negative electrode will be in the other half-cell.

The equation for the overall cell reaction is found by adding the two half-equations. Worked Example 9.2.1 shows you how to use the electrochemical series to predict a cell reaction.

Worked example 9.2.1

PREDICTING THE OPERATION OF A GALVANIC CELL

A cell is made from $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ and $\text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s})$ half-cells under standard conditions and at 25°C . Use the electrochemical series to predict the overall cell reaction, identify the anode and cathode, and determine the direction of electron flow.	
Thinking	Working
Identify the two relevant half-equations in the electrochemical series.	$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) \quad E^\circ = +0.80$ $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s}) \quad E^\circ = -0.44 \text{ V}$
Identify the strongest oxidising agent (the species on the left of the series with the most positive E° value) and the strongest reducing agent (bottom right).	Because Ag^+ is higher on the left side of the table than Fe^{2+} , it is the strongest oxidising agent. Fe, being lower on the right side of the table than Ag, is the strongest reducing agent.
Write the two half-equations that will occur. The strongest oxidising agent will react with the strongest reducing agent. (Hint: The reduction equation has the most positive E° value and the oxidation equation has the most negative E° value.)	Reduction: $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$ Oxidation: $\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$ Because this is the oxidation reaction, the half-equation should be written in reverse.
Write the overall cell equation.	Multiply the Ag^+/Ag half-cell equation by two so that the number of electrons in each half-equation is equal, and then add the two half-equations together: $\begin{array}{r} [\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})] \times 2 \\ \text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \\ \hline 2\text{Ag}^+(\text{aq}) + \text{Fe}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \text{Fe}^{2+}(\text{aq}) \end{array}$
Identify the anode and the cathode in this cell. The anode is the electrode at which oxidation occurs. The cathode is the electrode at which reduction occurs.	The silver electrode will be the cathode and the iron electrode will be the anode.

i Strong reducing agents donate electrons more readily than weak ones.

Strong oxidising agents accept electrons more readily than weak ones.

Strong reducing agents have weak conjugate oxidising agents.

Strong oxidising agents have weak conjugate reducing agents.

Determine the polarities of the electrodes and the direction of electron flow in the cell.

The anode is negative; the cathode is positive.

Electrons flow from the negative electrode (anode) to the positive electrode (cathode) as shown in Figure 9.2.6.

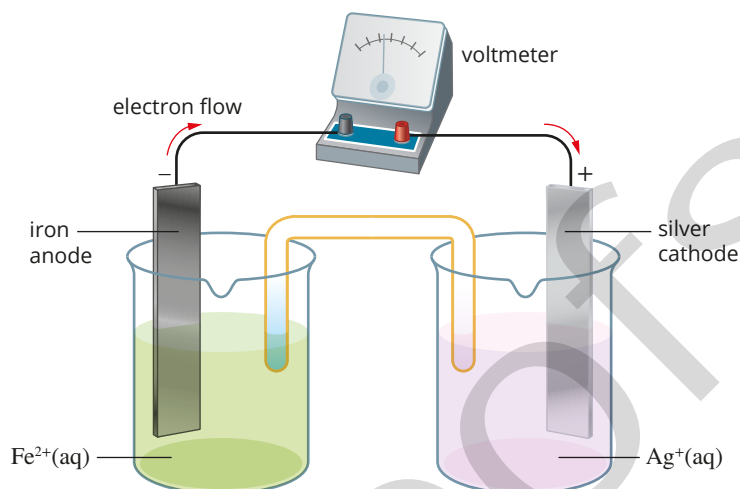


FIGURE 9.2.6 A cell containing Fe^{2+}/Fe and Ag^{+}/Ag half-cells

Worked example: Try yourself 9.2.1

PREDICTING THE OPERATION OF A GALVANIC CELL

A cell is made from $\text{Sn}^{2+}(\text{aq})/\text{Sn}(\text{s})$ and $\text{Ni}^{2+}(\text{aq})/\text{Ni}(\text{s})$ half-cells under standard conditions and at 25°C . Use the electrochemical series to predict the overall cell reaction, identify the anode and cathode, and determine the direction of electron flow.

Calculating the voltage of a cell

The maximum potential difference of a cell under standard conditions is the difference between the E° values of its two half-cells. It is defined as follows:

$$\text{cell potential difference} = E^{\circ} \text{ of half-cell containing the oxidising agent} \\ - E^{\circ} \text{ of half-cell containing the reducing agent}$$

An easy way to remember this for galvanic cells is:

$$\text{cell potential difference} = \text{higher half-cell } E^{\circ} - \text{lower half-cell } E^{\circ}$$

For example, the maximum cell voltage of a cell constructed from $\text{Ag}^{+}(\text{aq})/\text{Ag}(\text{s})$ and $\text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s})$ half-cells under standard conditions can be calculated as follows:

$$\begin{aligned} \text{cell potential difference} &= \text{higher half-cell } E^{\circ} - \text{lower half-cell } E^{\circ} \\ &= E^{\circ}(\text{Ag}^{+}(\text{aq})/\text{Ag}(\text{s})) - E^{\circ}(\text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s})) \\ &= 0.80 - (-0.44) \\ &= 1.24 \text{ V} \end{aligned}$$

Note that because the standard electrode potentials are all determined under standard conditions, different values for the cell voltage are obtained under non-standard conditions.

As a galvanic cell discharges, the cell voltage eventually drops to zero as the reactants are consumed. A point will come when the forward reaction is going no faster than the reverse reaction, and a state of equilibrium is achieved. Electrons will stop flowing from the anode to the cathode and the cell is referred to as 'flat'.

i The easiest way to calculate the cell potential difference is to remember:

$$\text{cell potential difference} = \text{higher half-cell } E^{\circ} - \text{lower half-cell } E^{\circ}$$

9.2 Review

SUMMARY

- The standard hydrogen half-cell is used as the standard reference half-cell; its value is arbitrarily assigned as zero.
- The standard electrode potential or standard reduction potential (E°) of a half-cell is measured by connecting the half-cell to a standard hydrogen half-cell and measuring the voltage produced.
- The standard electrode potential gives a numerical measure of the tendency of a half-cell reaction to occur as a reduction reaction.
- Standard electrode potentials are used as the basis of the electrochemical series.
- In the electrochemical series, half-reactions are listed in order so that the strongest oxidising agent is at the top left of the series (with the most positive E° value) and the strongest reducing agent is at the bottom right (with the most negative E° value).
- The electrochemical series is valid for standard conditions; that is, gas pressures of 100 kPa and solution concentrations of 1.00 mol L⁻¹. Standard electrode potentials are measured at 25°C.
- The relative strengths of oxidising and reducing agents can be determined by comparing standard electrode potentials, and these can be used to predict half-cell and overall cell reactions.
- The maximum potential difference of a cell under standard conditions = E° of half-cell containing the oxidising agent – E° of half-cell containing the reducing agent
or, more simply: cell potential difference = higher half-cell E° – lower half-cell E°
- For a spontaneous reaction to occur, an oxidising agent (on the left of the electrochemical series) must react with a reducing agent (on the right) that is lower in the series.

KEY QUESTIONS

- 1 A galvanic cell was constructed from Al³⁺(aq)/Al(s) and Pb²⁺(aq)/Pb(s) half-cells. Use the electrochemical series to predict the:
 - a oxidation and reduction half-equations
 - b overall cell reaction
 - c identity of the anode and cathode.
- 2 Draw a labelled diagram of a cell formed from Cl₂(g)/Cl⁻(aq) and Sn²⁺(aq)/Sn(s) half-cells. Use the electrochemical series to indicate the:
 - half-cell reactions
 - anode and cathode
 - direction of electron flow
 - electrode polarities (which electrode is positive and which is negative)
 - directions of flow of the anions and cations in the salt bridge
 - overall reaction.
- 3 Repeat Question 2 for the cells formed from the following half-cells.
 - a Fe³⁺(aq)/Fe²⁺(aq) and H⁺(aq)/H₂(g)
 - b Cl₂(g)/Cl⁻(aq) and Pb²⁺(aq)/Pb(s)
- 4 Calculate the cell potential difference for each of the cells in Questions 1–3.

9.3 Predicting direct redox reactions

The electrochemical series provides a ranking of the relative strengths of oxidising and reducing agents.

In this section, you will see that you can apply your understanding of the electrochemical series to predict the likelihood of a redox reaction taking place when different chemicals are combined.

PREDICTING REACTIONS

If the contents of the half-cells of a galvanic cell were mixed, the reactants would react directly. Energy would be released as heat rather than as electrical energy. Reactions that occur in galvanic cells or when chemicals are directly mixed are described as naturally occurring reactions, or spontaneous reactions.

In the last section, you saw that in a galvanic cell the strongest oxidising agent in the cell reacts with the strongest reducing agent. In other words, the higher half-reaction (the one with the most positive E° value) in the electrochemical series occurs in the forward direction (as reduction) and the lower reaction (the one with the most negative E° value) occurs in the reverse direction (as oxidation).

This principle applies equally to redox reactions that occur when reactants are mixed directly.

As shown in Figure 9.3.1, for a spontaneous reaction to occur, an oxidising agent (on the left of the electrochemical series) must react with a reducing agent (on the right) that is lower in the electrochemical series.

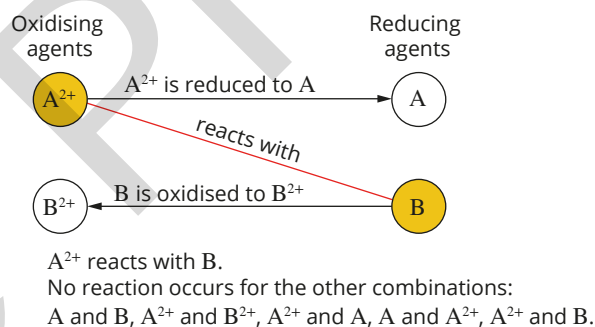


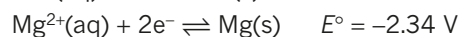
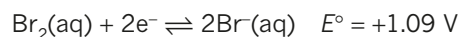
FIGURE 9.3.1 Oxidising agents only react significantly with reducing agents that are lower in the electrochemical series.

i With half-equations arranged in order of increasing reducing agent strength, you can predict that a spontaneous reaction will occur by looking for substances that are arranged in a top-left/bottom-right position.

Worked example 9.3.1

PREDICTING DIRECT REDOX REACTIONS

Consider the following equations that appear in the order shown in the electrochemical series.



Use the electrochemical series to predict the effect of mixing:

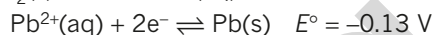
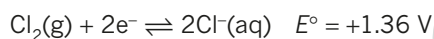
- $\text{Br}_2(\text{aq})$ and $\text{Mg}^{2+}(\text{aq})$
- $\text{Mg}^{2+}(\text{aq})$ and $\text{Ni}(\text{s})$
- $\text{Ni}^{2+}(\text{aq})$ and $\text{Mg}(\text{s})$.

Thinking	Working
<p>Identify the two relevant half-equations in the electrochemical series.</p> <p>Predict whether or not a reaction occurs. A chemical species on the left (an oxidising agent) of the electrochemical series reacts with a chemical species on the right (a reducing agent) that is lower in the series.</p> <p>Write the overall equation.</p>	<p>a $\text{Br}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-(\text{aq}) \quad E^\circ = +1.08 \text{ V}$ $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg}(\text{s}) \quad E^\circ = -2.36 \text{ V}$ No reaction occurs because both $\text{Br}_2(\text{aq})$ and $\text{Mg}^{2+}(\text{aq})$ are oxidising agents.</p> <p>b $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{s}) \quad E^\circ = -0.24 \text{ V}$ $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg}(\text{s}) \quad E^\circ = -2.36 \text{ V}$ No reaction occurs because the oxidising agent, Mg^{2+}, is below the reducing agent, Ni, in the electrochemical series.</p> <p>c $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{s}) \quad E^\circ = -0.24 \text{ V}$ $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg}(\text{s}) \quad E^\circ = -2.36 \text{ V}$ A reaction occurs because the oxidising agent, Ni^{2+}, is above the reducing agent, Mg, in the electrochemical series.</p> <p>The higher half-equation occurs in the forward direction:</p> $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$ <p>The lower half-equation occurs in the reverse direction:</p> $\text{Mg}(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{e}^-$ <p>The overall reaction equation is found by adding the half-equations:</p> $\text{Ni}^{2+}(\text{aq}) + \text{Mg}(\text{s}) \rightarrow \text{Ni}(\text{s}) + \text{Mg}^{2+}(\text{aq})$

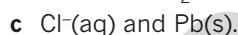
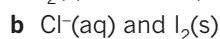
Worked example: Try yourself 9.3.1

PREDICTING DIRECT REDOX REACTIONS

Consider the following equations that appear in the order shown in the electrochemical series:



Use the electrochemical series to predict the effect of mixing:



Predicting cell reactions can also be considered from cell potential differences calculated as shown in section 9.2. If the cell potential for an overall reaction is a positive value, that reaction should occur spontaneously. If the cell potential of a proposed reaction is a negative value, that reaction will not occur spontaneously.

LIMITATIONS OF PREDICTIONS

The standard half-cell potentials given in the electrochemical series are measured under standard conditions. As you would expect, half-cell potentials can vary under other conditions.

When conditions are very different from standard conditions, the order of half-reactions in the electrochemical series may also be different, and predictions of reactions based on the standard half-cell potentials may not be reliable.

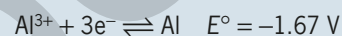
It is also important to remember that the electrochemical series gives no information about the rate at which reactions occur.

CHEMFILE

The thermite reaction

The thermite reaction is a highly exothermic reaction between powdered aluminium and iron(III) oxide.

The two relevant half-equations for this reaction, listed in their order in the electrochemical series are:



A spontaneous reaction is predicted to occur because the oxidising agent, Fe^{3+} , is above the reducing agent, Al, in the series. (Even though the actual reaction here does not occur in aqueous solution, and under standard conditions, you can still compare the electrode potentials to determine the stronger reducing agent.)

The thermite reaction releases so much heat that it is enough to melt the iron that is produced. One use for the thermite reaction is for welding together railway tracks (Figure 9.3.2).



FIGURE 9.3.2 Thermite welding of railway tracks

9.3 Review

SUMMARY

- The relative strength of oxidising and reducing agents can be determined by comparing standard electrode potentials, and these can be used to predict the tendency of a reaction to occur, both in galvanic cells and in direct reactions.
- For a spontaneous reaction to occur, an oxidising agent (on the left of the electrochemical series) must react with a reducing agent (on the right) that is lower in the series.
- Overall equations for redox reactions can be obtained by adding half-equations.
- When reactants react in a galvanic cell, chemical energy is transformed into electrical energy. However, when they react directly, their chemical energy is transformed into heat energy.
- The standard half-cell potentials in the electrochemical series are measured under standard conditions. Under other conditions, the order of half-reactions may be different, and predictions based on the electrochemical series may not be reliable.

KEY QUESTIONS

- 1 Which one of the following metals would you expect to be coated with lead when immersed in a solution of lead(II) nitrate?
A Copper
B Cobalt
C Silver
D Gold
- 2 Which one of the following species would react with $\text{H}_2\text{S}(\text{g})$ but not with $\text{H}_2\text{O}(\text{l})$ under standard conditions?
A $\text{Cl}_2(\text{g})$
B $\text{Mg}(\text{s})$
C $\text{Ag}^+(\text{aq})$
D $\text{Cu}(\text{s})$
- 3 Using the electrochemical series, predict whether a reaction will occur in the following situations. If a reaction does occur, write the overall equation for the reaction.
 - a Chlorine gas is bubbled into a solution containing bromide ions.
 - b Chlorine gas is bubbled into a solution containing iodide ions.
 - c A bromine solution is added to a solution containing chloride ions.
 - d A bromine solution is added to a solution containing iodide ions.
- 4 A reaction occurs when a strip of zinc metal is placed in a silver nitrate solution.
 - a Write the overall equation for the reaction.
 - b Describe the energy change that takes place in this reaction.
- 5 Iron nails are placed into 1 mol L^{-1} solutions of CuSO_4 , MgCl_2 , $\text{Pb}(\text{NO}_3)_2$ and ZnCl_2 . Use the electrochemical series to identify in which solution(s) you would expect a coating of a metal other than iron to appear on the nail.

9.4 Everyday sources of power

The battery was invented by Alessandro Volta in 1800. More than two centuries later, cells and batteries are a common power source for many household and industrial applications. Cells and batteries can be used as fixed energy storage systems, such as in solar energy systems, burglar alarms and smoke detectors. They are also used extensively in portable applications, including mobile phones, watches, digital cameras and laptop computers. The portability of these devices relies on these sources of electrical energy.

Cells and batteries use spontaneous redox reactions as the source of energy. In this section, you will look at the three main types of cells in use and how chemical reactions in these cells are used to produce electricity for everyday applications.

The three basic types of cells are:

- **primary cells**, which are disposable and designed not to be recharged
- **secondary cells**, which are rechargeable and designed to be reused many times
- **fuel cells**, which continuously produce electricity for as long as fuel is fed into the cells.

Primary cells, secondary cells and fuel cells are all types of galvanic cells.

PRIMARY CELLS

Common commercial **alkaline cells**, such as those you would usually use in a torch or a remote control, are **non-rechargeable cells** (Figure 9.4.1). They 'go flat' when most of the reactants are used up, the cell reaction reaches equilibrium, and you have to buy a replacement.



FIGURE 9.4.1 Non-rechargeable alkaline cells are used to power many devices, including torches, smoke detectors and calculators. They are discarded once they go flat.

EXTENSION

Primary cells—alkaline cells

Following World War II, an expanding range of electrical appliances became available that required small, high-capacity power sources. The earlier types of cells were unable to meet these demands, so the alkaline cell was developed in the late 1960s.

Figure 9.4.2 shows the construction of an alkaline cell. This cell is similar to the simple galvanic cells discussed earlier in this chapter, but has been designed so the two half-reactions occur in separate places within the one container. A potassium hydroxide electrolyte performs the same function as a salt bridge in the simple cells.

An alkaline cell needs less electrolyte than a dry cell, which it has largely replaced for household use. The smaller quantity of electrolyte allows more reactant to be included. A typical D size alkaline cell contains about 40 g of manganese dioxide, compared with 25 g in a dry cell of equivalent size.

The following reactions occur in an alkaline cell.

- At the anode (–), zinc powder around the central metal rod is oxidised and reacts with hydroxide ions, forming zinc hydroxide:

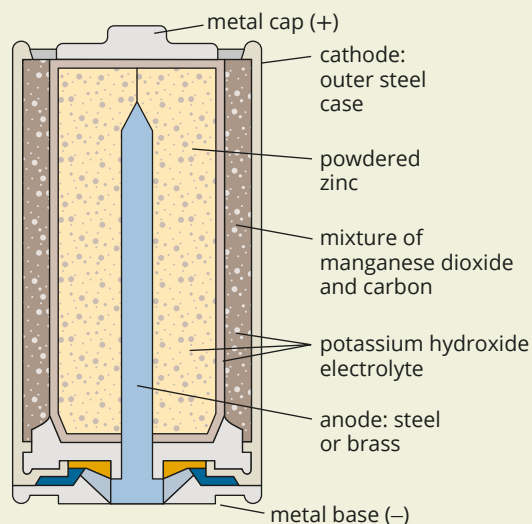
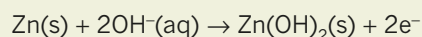


FIGURE 9.4.2 Construction of an alkaline cell

- At the cathode (+), manganese dioxide is reduced:
$$2\text{MnO}_2\text{(s)} + \text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3\text{(s)} + 2\text{OH}^{\text{(aq)}}$$

Alkaline cells are especially cost-effective in torches, flashguns and motorised toys, where high currents are needed intermittently. The cell produces about 1.5V. Once the reaction in the cell reaches equilibrium, the cell is 'flat', and cannot be used again.

Cells that cannot be recharged are called primary cells. In primary cells, the products slowly migrate away from the electrodes or are consumed by side reactions occurring in the cell, preventing the cells from being recharged.

CHEMFILE

Powering the Overland Telegraph

One of the first primary cells in widespread use in the 19th century was called the Leclanché cell. It had a similar overall cell reaction to the reaction in alkaline cells.

Leclanché cells were one of the sources of power for the Australian Overland Telegraph Line, one of the great engineering feats of 19th-century Australia. The 3200 km telegraph line was completed in 1872 and connected Darwin in the Northern Territory with Port Augusta in South Australia, allowing fast communication between Australia and the rest of the world. An additional section to Western Australia was added in 1877.



FIGURE 9.4.3 The Alice Springs telegraph station, built in 1872

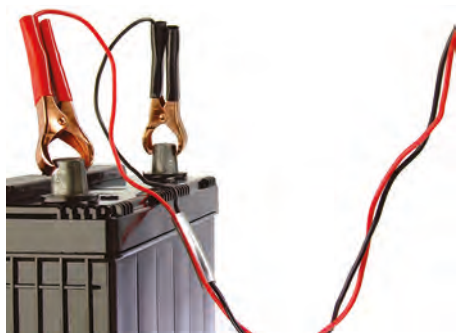


FIGURE 9.4.4 Charging a secondary battery involves connecting the positive terminal of a charger to the battery's positive electrode and the negative electrode of the charger to the battery's negative electrode.

SECONDARY CELLS

Rechargeable cells such as **lithium-ion cells** and **nickel–metal hydride cells**, are known as secondary cells or **accumulators**.

Rechargeable cells and batteries have become very popular and are found in mobile phones, laptop computers, cameras and portable power tools. They are also fundamental to the operation of electric vehicles and solar power energy storage systems.

Most types of rechargeable cells can undergo many hundreds of recharges. To recharge a cell, the cell reaction must occur in reverse: the products of the reaction must be converted back into the original reactants. This is done by connecting the cell to a 'charger', a source of electrical energy, which has a potential difference a little greater than the potential difference of the cell. The positive terminal of the charger is connected to the cell's positive electrode and the negative electrode of the charger to the cell's negative electrode (see Figure 9.4.4).

i Primary cells cannot be recharged, whereas secondary cells can be recharged by connecting them to an external source of electricity.

Electrical energy supplied by the charger is converted into chemical energy in the cell. In order for it to be possible to regenerate the reactants, the products formed in the cell during discharge must remain in contact with the electrodes in a convertible form.

The energy transformations in a secondary cell can be summarised as follows.

- When a secondary cell discharges, it acts as a galvanic cell, converting chemical energy into electrical energy.
- When the cell is recharged, it acts as a type of cell called an **electrolytic cell**. Electrical energy is transformed into chemical energy in an electrolytic cell. You will learn more about the operation of electrolytic cells in Chapter 10.

The energy transformations and redox processes that occur during the discharging and recharging of a secondary cell are summarised in Figure 9.4.5.

Discharging:

- acts as galvanic cell
- spontaneous reaction



Recharging:

- acts as electrolytic cell
- non-spontaneous reaction

FIGURE 9.4.5 Energy transformations in secondary cells

Secondary batteries—car batteries

Lead–acid batteries are the most widely used type of secondary cell. They are relatively cheap and reliable, provide high currents, and have a long lifetime.

Most people know the lead–acid battery simply as a car battery (Figure 9.4.6). It is used to start the car's engine and to operate the car's electrical accessories when the engine is not running. Once the engine starts, an alternator, which is run by the engine, provides electrical energy to operate the car's electrical system and recharge the battery.

Lead–acid batteries are also used for emergency light and power systems, for small-scale energy storage and to power some electric vehicles such as golf buggies and small fork lifts.

As shown in the diagram in Figure 9.4.7, a modern lead–acid battery is actually six separate cells connected together in series. The positive electrodes consist of a lead grid packed with lead(IV) oxide (PbO_2) while the negative electrodes consist of a lead grid packed with powdered lead. A solution of sulfuric acid, of about 4 mol L^{-1} concentration, acts as the electrolyte.



FIGURE 9.4.6 Lead–acid batteries are used to start cars, trucks and motorcycles.

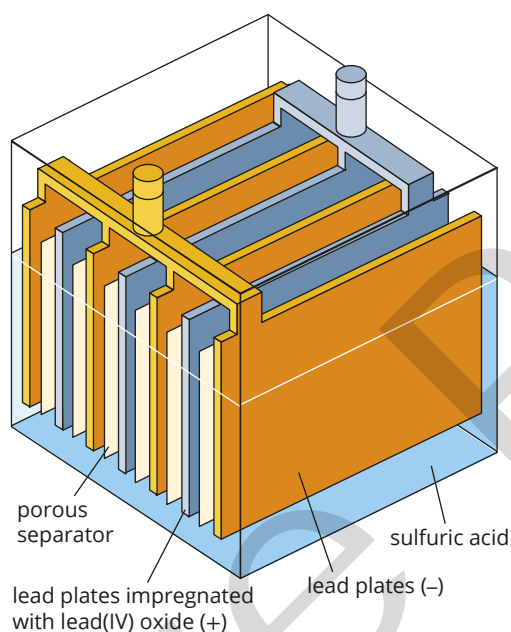


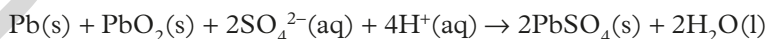
FIGURE 9.4.7 Construction of a lead–acid battery

Each cell has a potential difference of just over 2 V. A car battery has six of these cells connected in series, giving a total potential difference of about 12 V.

The following reactions occur in a lead–acid battery as it produces electricity.

- At the anodes (–), lead is oxidised to Pb^{2+} ions:
 $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$
- At the cathodes (+), lead(IV) oxide is reduced to Pb^{2+} ions:
 $\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$

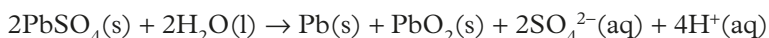
The two half-equations can be combined as an overall equation:



The product of both electrode reactions, lead(II) sulfate, forms as a solid on the surface of the electrodes. This enables the battery to be recharged.

To recharge the battery, the electrode reactions are reversed. The alternator, with a potential difference of about 14 V, is used to force electrons into the battery's negative terminal and draw them out at the positive terminal, in effect driving the spontaneous reaction backwards. The recharging process converts electrical energy into chemical energy.

The overall equation for the reaction as the battery recharges is:



Lithium-ion batteries

Some car manufacturers are beginning to equip cars with lithium-ion batteries instead of traditional lead–acid batteries. Lithium-ion batteries are much lighter, lowering the overall weight of a car and offering a slight improvement in fuel efficiency. Although more costly, lithium-ion batteries also last longer than lead–acid batteries, which means they need replacing less often.

Lithium-ion cells and batteries are also the power source of choice for many portable electronic products, including phones, notebook computers and digital cameras (Figure 9.4.8). They are light and powerful, and unlike ordinary alkaline cells, lithium-ion cells and batteries are not discarded when flat. Instead, they are secondary cells and can be recharged and reused.

Sony released the first commercial lithium-ion cells in 1991. Lithium's low weight and high reactivity had long been recognised as potentially useful in cells and batteries. However, while lithium's reactivity might be ideal, it also makes practical applications difficult. Lithium reacts with many everyday materials and can react explosively with water. As a consequence, the development of a lithium-based cell using a non-aqueous electrolyte has been a significant scientific as well as technological achievement.

Lithium-ion cells are designed principally to overcome the safety concerns surrounding the use of a strong reactant such as metallic lithium. Lithium-ion cells do not contain lithium in the metallic state; rather, the lithium is adsorbed into the lattice structure of a graphite electrode.

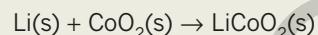
When a lithium-ion cell generates electricity, the following half-reactions occur.

- At the anode (–), oxidation of lithium generates electrons:

$$\text{Li(s)} \rightarrow \text{Li}^+ + \text{e}^-$$
 Once formed, Li^+ ions migrate into the electrolyte.
- At the cathode (+), the electrode material, which is usually a metal oxide such as cobalt oxide, accepts electrons. The product combines with Li^+ ions from the electrolyte and precipitates. For example:

$$\text{CoO}_2(\text{s}) + \text{Li}^+ + \text{e}^- \rightarrow \text{LiCoO}_2(\text{s})$$

The equation for the overall cell reaction is formed by adding the two half-equations:



A lithium-ion cell delivers a steady 3.6 V as it discharges. When a lithium-ion cell is discharging, the products of the reaction remain available within the cell. By supplying the discharged cell with electrical energy, the electrode reactions can be reversed and the reactants regenerated.

Although their complex internal structure makes them more expensive to manufacture, lithium ion cells are becoming increasingly popular because of their high energy density and low weight.



FIGURE 9.4.8 Lithium-ion power supplies are used in drones and radio-controlled models.

FUEL CELLS

The major limitation of the cells that have been examined so far is that they contain relatively small amounts of reactants. Furthermore, when the reaction reaches equilibrium, the cell must be discarded or recharged.

Cells can be constructed in which the reactants are supplied continuously, allowing constant production of electrical energy. These devices are called fuel cells.

i A key difference between a fuel cell and a primary or secondary cell is that the reactants are not stored in the fuel cell. They must be continuously supplied from an external source.

Fuel cells use the chemical energy of hydrogen or other fuels to cleanly and efficiently generate electricity. Even though fuel cell technology is still being developed, fuel cells can be used in numerous applications. These uses include as a source of power for transport (see Figure 9.4.9) and for emergency back-up power applications.

A fuel cell is a type of galvanic cell but, unlike the cells you studied previously in this chapter, fuel cells do not run down or need recharging. Electricity is produced for as long as fuel is supplied to them.

Efficiency of fuel cells

Fuel cells transform chemical energy directly into electrical energy, enabling efficient use of the energy released by spontaneous redox reactions. They are a useful source of continuous electricity and could be used to provide energy for vehicles, buildings and even cities. Energy losses such as those that occur in coal-fired power stations and combustion engines are avoided, with a consequential reduction in the volume of greenhouse gases produced.

Fuel cells are generally quoted as being 40–60% efficient, compared with efficiencies of 30–40% for thermal power stations and 25–30% for car engines, which involve a series of different energy transformations.

In addition, some modern fuel cells use the waste heat that they produce to make steam. This steam can be used for heating or to operate a turbine, thus raising the efficiency of the cells to up to 85%.

i Fuel cells have a much higher efficiency than thermal power stations because chemical energy is directly converted into electrical energy.

A fuel cell using hydrogen as a fuel produces electricity, water, heat and very small amounts of nitrogen dioxide and other emissions.

Although the basic principles behind the operation of a fuel cell were discovered in 1838, it was not until the 1950s that fuel cells were used for small-scale power production. Fuel cells, such as the one shown in Figure 9.4.10, were the main on-board power supply units and source of water during the Apollo space program that put humans on the Moon. An explosion in a fuel cell was responsible for the failure of the Apollo 13 mission.

Fuel cell design

Figure 9.4.11 shows a simplified diagram of the key parts of a hydrogen–oxygen fuel cell. The fuel cell has two compartments: one for the hydrogen gas and the other for the oxygen gas. The gas compartments are separated from each other by two porous electrodes and an electrolyte solution. The electrode at the hydrogen compartment is the anode; the electrode at the oxygen compartment is the cathode.



FIGURE 9.4.9 A hydrogen fuel cell for an electric bicycle. The hydrogen bicycle operates like a standard electric bicycle, but the battery lasts three times longer.

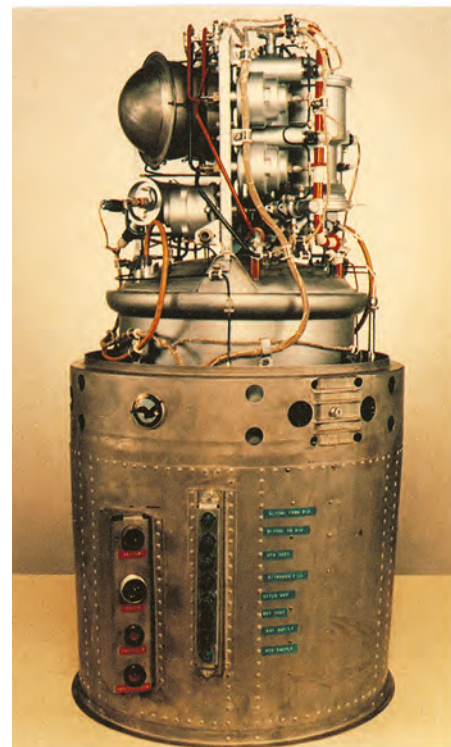


FIGURE 9.4.10 Fuel cells like this were used to supply electricity for the Apollo space program (1969–72). Fuel cells were also used in the later space shuttles.

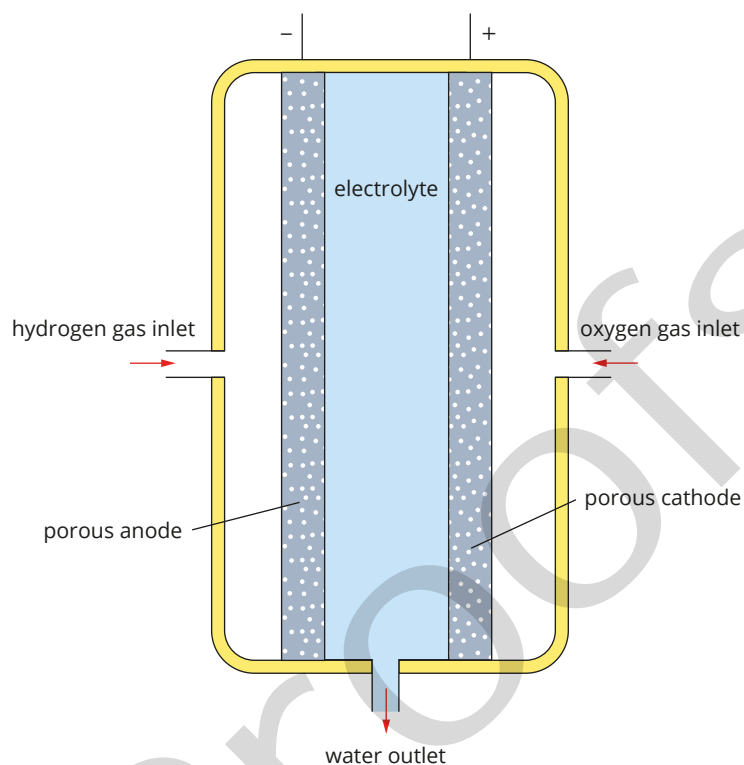
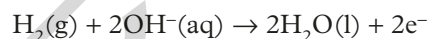


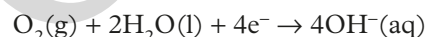
FIGURE 9.4.11 A simplified diagram showing the key parts of a hydrogen–oxygen fuel cell

The type of fuel cell used in the Apollo program used potassium hydroxide solution as the electrolyte and the cell operated at about 250°C. Because the fuel cell uses potassium hydroxide for the electrolyte, it is commonly referred to as an alkaline fuel cell. Alkaline fuel cells are still used in the space program today.

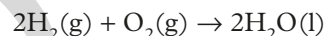
- At the anode (–), hydrogen gas (the ‘fuel’) is oxidised by reacting with hydroxide ions from the electrolyte:



- At the cathode (+), oxygen gas is reduced:



The overall equation for the reaction is:



Each cell produces about 1 V. Higher voltages are obtained by connecting a number of fuel cells in series to form a battery or fuel cell stack. The only by-product is water, and heat is also given off.

A range of different fuel cells has been developed, using different electrolytes, electrodes and operating temperatures.

The nature of the electrodes is crucial to the efficiency of a fuel cell. The electrodes must be both conducting and porous to allow the hydrogen and oxygen to come into contact with the ions in the electrolyte and to allow the redox half-reactions to occur at their surface. The size of the current that can be drawn from a fuel cell depends on the surface area of the electrodes.

Catalysts are used to enhance the rate of reaction and the current that can be produced from a cell. The catalyst incorporated in the anode increases the rate of oxidation of the fuel gas. Platinum metal is commonly used as a catalyst at this electrode. The cathode catalyst, which increases the rate of the reduction half-reaction, can be made from a different material, such as nickel powder or a nanomaterial.

i Fuels cells contain porous electrodes that allow reactants to diffuse through them to react with ions in the electrolyte. They often contain catalysts to increase the rate of reaction.

THE HYDROGEN ECONOMY

Some scientists predict that, in the future, hydrocarbons will be replaced by hydrogen as the principal source of energy for transport and other purposes (the **hydrogen economy**). This would mean a drastic reduction in the production of greenhouse gases and other pollutants without affecting your quality of life. In the hydrogen economy, fuel cells are seen as a replacement for the internal combustion engine.

The widespread use of hydrogen as a source of energy presents special challenges and issues, in terms of its production, distribution, storage and safety.

Hydrogen production and storage

A fuel cell using hydrogen can be described as a ‘zero-emission’ device because water is almost the only product apart from electricity and heat. However, unless the hydrogen fuel is produced using renewable energy, the production of hydrogen can result in significant levels of greenhouse gases and other pollutants. To some extent, this negates the benefits of the use of fuel cells. At present, almost 95% of hydrogen is produced from fossil fuels, such as natural gas, oil and coal.

Alternative ways of producing hydrogen are being explored. At present, there are only two practical methods of generating hydrogen without producing carbon dioxide:

- using electrical energy to convert water to hydrogen. Electricity can be generated from renewable sources such as solar-power farms and wind farms (You will look at the chemical principles involved in the process of converting electrical energy to chemical energy in Chapter 10.)
- collecting **biogas** from landfill sites and converting the methane in the gas to hydrogen.

Widespread adoption of hydrogen as the primary fuel for powering vehicles and providing electricity for industrial and domestic applications would also require massive expenditure on infrastructure. Changes to pipelines and filling stations, as well as improvements in hydrogen storage methods, would be required.

The established methods of hydrogen storage in cars, trucks and buses are as liquid hydrogen or compressed hydrogen. Both storage methods provide substantially less energy per litre than the equivalent volume of a liquid hydrocarbon fuel such as petrol. Scientists are investigating alternative methods of storing hydrogen, including adsorption to the surface of materials such as metal hydrides. These storage methods offer considerable promise but require further development.

Figure 9.4.14 (page xxx) shows a vision for the future use of hydrogen.

Australia is a member of the International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE). This organisation was established in 2003 to accelerate the transition to a hydrogen economy. IPHE provides a mechanism for member countries to organise, coordinate and implement research and activities related to hydrogen and fuel cell technologies. Each country has committed to collaborating to advance hydrogen and fuel cell technologies in the marketplace in an effort to improve energy supply and the environment.

CHEMFILE

Fuel cells around us

Some types of breathalysers use fuel cell technology to measure blood alcohol levels. In this fuel cell, ethanol is oxidised and the electricity generated indicates the blood alcohol level (Figure 9.4.12).



FIGURE 9.4.12 Hand-held breathalysers are a type of fuel cell.

Fuel cells are also found in nature. The electric eel, which grows to more than 1 metre in length, has a natural battery made of specialised fuel cells within its body (Figure 9.4.13). The fuel for each cell is the food consumed by the eel and the oxidising agent is oxygen. Each cell generates about 1.5 V, yielding a total voltage from the head of the eel to its tail of more than 300 V.



FIGURE 9.4.13 Electric eels use electricity for several reasons. Low pulses of electrical discharge are emitted by the eel and then bounce back from passing objects to be detected by special electroreceptors on the skin. In this way, the eel navigates and locates its prey. High-intensity electrical discharges can also be used to stun or kill prey or as a form of defence.

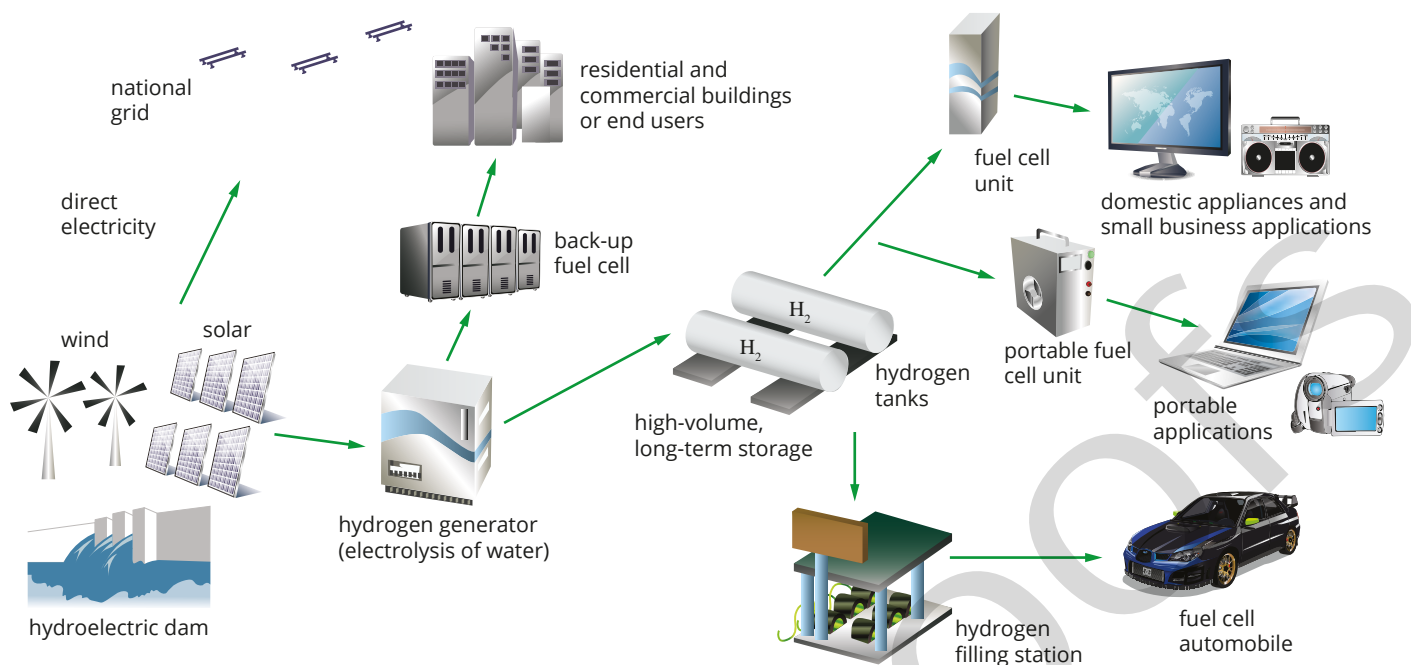


FIGURE 9.4.14 A view of future energy production based on the use of hydrogen

ADVANTAGES AND DISADVANTAGES OF FUEL CELLS

Scientists are striving to reduce the overall costs of fuel cells and to improve the electric current that can be drawn from them by increasing the rate of reaction at the electrodes. As described above, various types of fuel cells have been developed and tested, using a number of different fuels, electrolytes and catalysts.

Table 9.4.1 lists some of the advantages and disadvantages of fuel cells.

TABLE 9.4.1 Advantages and disadvantages of fuel cells

Advantages	Disadvantages
<ul style="list-style-type: none"> • Fuel cells convert chemical energy directly to electrical energy. This is more efficient than the series of energy conversions that takes place in power stations that burn fossil fuels: chemical energy → heat energy → mechanical energy → electrical energy. • Hydrogen fuel cells produce water and heat as by-products. No greenhouse gases, such as carbon dioxide, are released. • Fuel cells will generate electricity as long as the fuel is supplied. Conventional batteries need to be recharged or replaced. • Fuel cells can use a variety of fuels. • Electricity can be generated on-site and users are not reliant on connection to an electricity grid. Waste heat can be used to heat water for a hot water system or provide heating for a home during winter. 	<ul style="list-style-type: none"> • Fuel cells require a constant fuel supply. • Fuel cells are expensive. They are still a developing technology, and are not being made in large numbers so there are no economies of scale as there are in other industries. • Some types of fuel cell use expensive electrolytes and catalysts. • The use of fuel cells in transport will require an extensive network of hydrogen filling stations before it can become widespread. • At present, the hydrogen used in many fuel cells is mainly sourced from fossil fuels. This process involves energy losses and generates greenhouse gases. • There are significant issues associated with the storage of hydrogen fuel.

APPLICATIONS OF FUEL CELLS

Most major vehicle manufacturers are investigating the use of fuel cells as an alternative to the internal combustion engine, given that fuel cells have better fuel efficiency, lower emissions of greenhouse gases and other pollutants, and do not rely on oil (Figure 9.4.15).

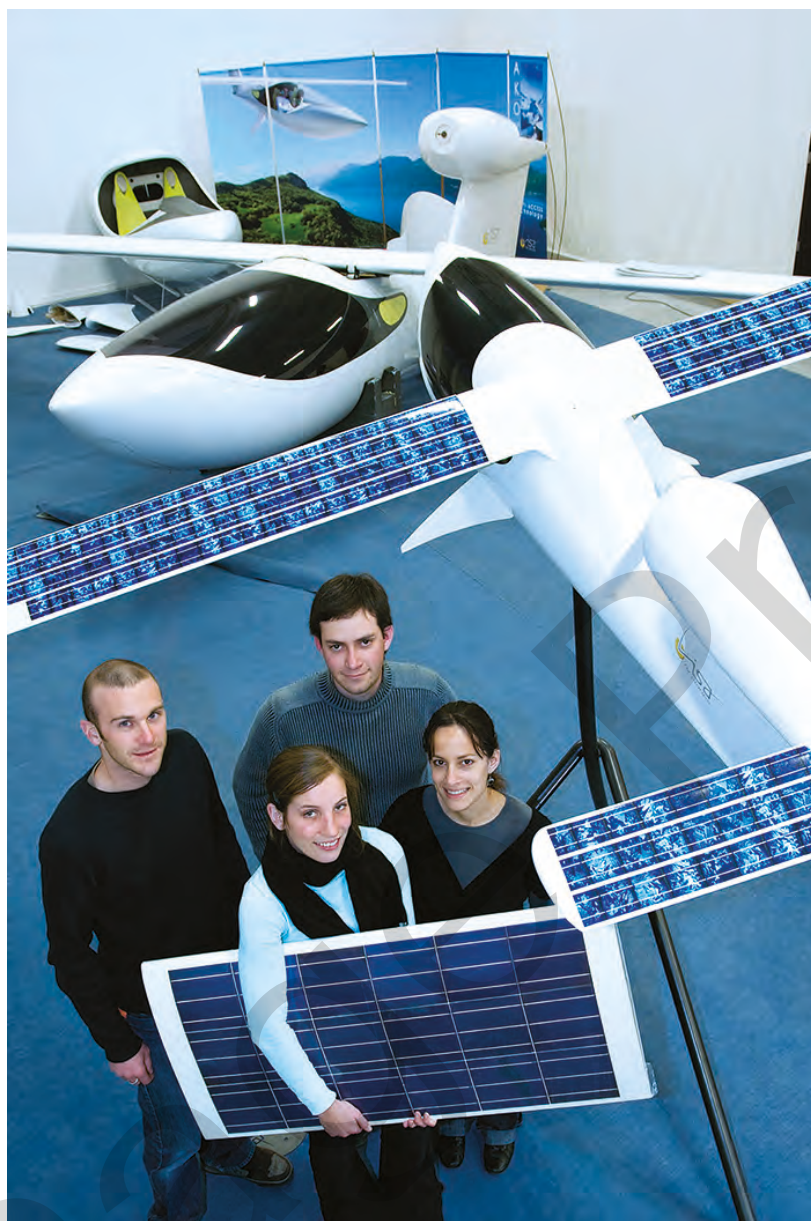


FIGURE 9.4.15 Technicians with a prototype aircraft powered by a combination of solar cells, which power the on-board electronics, and a hydrogen fuel cell, which powers the electric engine

Apart from their use in transport, the use of fuel cells is small at present but growing rapidly.

- A 1.3 MW power plant in Italy uses phosphoric acid fuel cells that are powered by hydrogen from steam reforming of natural gas (Figure 9.4.16).
- A 59 MW power plant began operation in South Korea in 2014, providing power and heat for local homes.
- One supermarket chain in the United States has ordered fuel cells to power its fleet of 1700 forklift vehicles.
- Silicon Valley technology companies in California, USA, are installing fuel cells as a stable, sustainable source of power.



FIGURE 9.4.16 Interior of the PRODE fuel cell power station in Milan, Italy, which began operating in 1992. The cells use hydrogen as the fuel and phosphoric acid as the electrolyte. The fuel cells can produce up to 1.3 MW of electricity.

9.4 Review

SUMMARY

- Primary, secondary and fuel cells are examples of galvanic cells, converting chemical energy directly into electrical energy.
- Primary cells cannot be recharged whereas secondary cells can be recharged by connecting them to an external source of electricity.
- For a cell to be rechargeable, the products of the discharge reaction have to remain in contact with the electrodes.
- During the recharging of a secondary cell, the equation for the reaction that occurs during the recharging of a secondary cell is the reverse of the equation for the cell discharging.
- When a secondary cell discharges it acts as a galvanic cell, releasing electrical energy; when it is recharged, it acts as an electrolytic cell, converting electrical energy to chemical energy
- Fuel cells are devices in which the reactants are supplied continuously, allowing constant production of electrical energy.
- Electricity generation using fuel cells is more efficient than if the electricity were generated by the combustion of the same fuel.
- The emissions of greenhouse gases from a fuel cell are much less than if the fuel were burnt in a power station or vehicle.
- Some scientists predict that fuel cells will play a key role in the transition from a dependence on fossil fuels for energy to a hydrogen economy.

KEY QUESTIONS

- 1 Describe the key difference between a primary cell and a secondary cell.
- 2 Most modern mobile phones contain lithium-ion cells. Select the correct statement about the process that occurs when a phone battery is recharged.
 - A A non-spontaneous reaction occurs and the lithium-ion cell acts as an electrolytic cell.
 - B A non-spontaneous reaction occurs and the lithium-ion cell acts as a galvanic cell.
 - C A spontaneous reaction occurs and the lithium-ion cell acts as an electrolytic cell.
 - D A spontaneous reaction occurs and the lithium-ion cell acts as a galvanic cell.
- 3 Which one or more of the following features do secondary cells and fuel cells have in common as they produce electricity?
 - A A catalyst is used to increase reaction rate.
 - B Cations in the electrolyte move towards the cathode.
 - C The anode is negative.
 - D The cathode is constructed from a porous material.
 - E Oxidation occurs at the cathode.
 - F The oxidising agent is a gas.
 - G Chemical energy is converted into electrical energy.
- 4 Which one of the following is a correct statement about what happens in a hydrogen–oxygen fuel cell?
 - A Hydrogen gas is oxidised at the anode.
 - B Electrons flow through the external circuit from cathode to anode.
 - C Solid, impermeable electrodes are required to prevent contact between reactants and the electrolyte.
 - D Oxygen gas is oxidised at the anode.
- 5 In a silver–zinc button cell, the cell reaction is:
$$\text{Zn(s)} + \text{Ag}_2\text{O(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Zn(OH)}_2\text{(s)} + 2\text{Ag(s)}$$
The zinc acts as the anode and the cell contains a potassium hydroxide electrolyte. Write a half-equation for the reaction occurring at the:
 - a anode
 - b cathode.

9.5 Corrosion

The reactions that occur when metals corrode are redox reactions. The costs associated with corroding metals are substantial, especially because iron, which is particularly prone to corrosion in the presence of water and oxygen, is so widely used as a structural material for buildings, bridges, gas and water pipes and ships. The effect of corrosion in water pipes is evident in the pumping system shown in Figure 9.5.1.



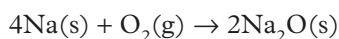
FIGURE 9.5.1 Corrosion is causing water to leak in these pipes in a pumping system.

In Australia, about \$50 billion (approximately 3% of gross domestic product) is spent each year in an effort to prevent metals from corroding and replacing metal that has corroded. In spite of such efforts, steel structures continue to corrode, eventually producing the familiar orange-brown flakes known as rust, although corrosion prevention methods can slow down the rate of corrosion considerably.

In this section, you will use your knowledge of redox chemistry and galvanic cells to consider the chemistry of corrosion. You will look at the redox reactions involved in corrosion both in the presence of water and in the absence of water.

DRY CORROSION

Direct reaction with oxygen in the air to form a metal oxide is known as **direct corrosion** or **dry corrosion**. Sodium is so reactive that it must be stored under oil to prevent contact with oxygen. The following equation represents the dry corrosion of sodium:



Dry corrosion of aluminium forms a tough, impervious coating of aluminium oxide (Al_2O_3), which protects the metal underneath from further contact with oxygen. The aluminium window frame in Figure 9.5.2 is lightweight and corrosion resistant. Therefore, it is an excellent material in situations where maintenance would be difficult.

Iron is much less reactive than sodium or aluminium; dry corrosion of iron is slow at room temperatures. When iron does corrode, it forms a coating that flakes off readily, leaving the metal underneath exposed to further corrosion.



FIGURE 9.5.2 An aluminium window frame is resistant to corrosion and is a useful material in situations where maintenance would be difficult.

WET CORROSION

The presence of moisture accelerates the corrosion of iron. This process is known as **wet corrosion**. The best-known example of wet corrosion is the formation of rust as a flaky, brown-red coating on iron.

Wet corrosion can occur in moist air or by direct immersion in water. Several factors affect the rate at which wet corrosion occurs. Consider the observations represented in Figure 9.5.3.

Each of these observations gives you information about the factors that influence the rate of wet corrosion of iron. In general, corrosion is accelerated by:

- the presence of water
- impurities such as salt and acidic pollutants that dissolve in the water.

However, corrosion can be reduced when the iron is alloyed with certain other materials or when it has a protective coating. You will see this later when the methods of prevention of corrosion are discussed.

In order to understand the process of wet corrosion of iron, and how it can be prevented, it is useful to consider the reactions occurring as a form of galvanic cell, with an anode (oxidation) and a cathode (reduction). The conducting iron allows for electrons to travel between the anode (anodic site) and the cathode (cathodic site).

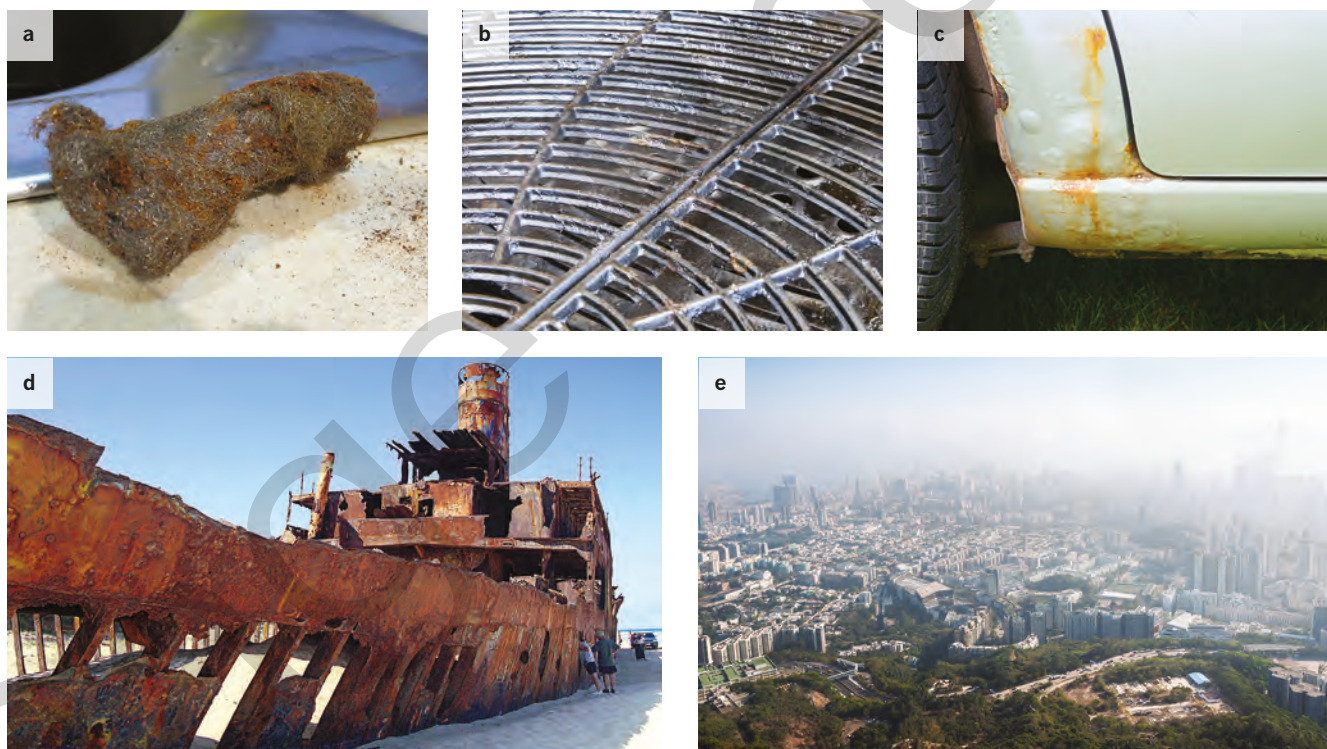
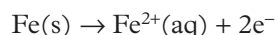


FIGURE 9.5.3 Wet corrosion. (a) A piece of steel wool (iron) does not corrode on supermarket shelves. However, once it becomes wet through use, it corrodes quickly. (b) An iron barbecue grill that has been coated with grease shows little sign of corrosion, even after being exposed to the rain for some time. (c) Rust in a car generally starts inside door frames, under mudguards, or in places where the paint has been chipped. (d) Shipwrecks corrode rapidly and will eventually disintegrate. (e) Corrosion occurs more rapidly in cities with a pollution problem, particularly where the pollutants include acidic oxides such as nitrogen dioxide and sulfur dioxide.

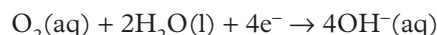
Wet corrosion process

Rust is a hydrated oxide of iron with the formula $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. There can be 1–3 water molecules associated with the iron oxide in its structure. An understanding of the steps involved in corrosion helps scientists to identify methods of corrosion prevention.

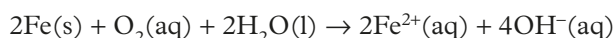
Step 1: Iron is oxidised to form Fe^{2+} ions at one region on the iron surface:



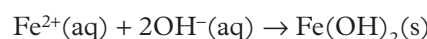
At the same time at another region on the surface, using the electrons produced by the oxidation process, oxygen is reduced in the presence of water to hydroxide ions:



The overall equation for step 1 is:



Step 2: The formation of a precipitate of iron(II) hydroxide:



Steps 1 and 2 of the wet corrosion process are summarised in Figure 9.5.4.

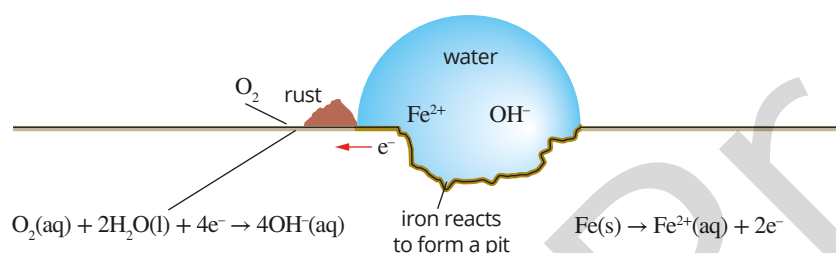
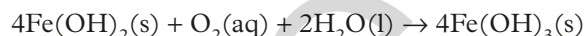


FIGURE 9.5.4 During wet corrosion, electrons are transferred through the iron from the area where oxidation occurs to the area where reduction occurs. Ions flow through the water droplets.

Step 3: Further oxidation of iron(II) hydroxide occurs in the presence of oxygen and water to produce iron(III) hydroxide, a red-brown precipitate:



Step 4: In air, the iron(III) hydroxide loses water to form hydrated iron(III) oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$), which is known as rust.

The porous rust easily flakes off the surface of the iron, exposing the iron underneath to further oxidation.

The wet corrosion of iron is accelerated if the water contains dissolved ions. This is particularly evident in coastal areas where iron objects are exposed to seawater. The presence of dissolved ions in the water increases its conductivity, which results in an increase in the rate of iron corrosion.

Prevention of corrosion

There are several ways to protect iron and steel structures against corrosion. These depend on the environment in which the structure is located, the design and intended use of the structure, and the relative costs of various protection measures. All methods will prevent one of the processes described above from happening. If you stop one process, then you will stop the overall rusting process.

The simplest way relies on the creation of a barrier between the iron and oxygen and water to provide a surface protection. Other methods are based on an understanding of the electrochemical nature of corrosion.

Surface protection

Surface protection involves covering the surface of the iron to prevent contact with oxygen and moisture. Materials such as paint and plastic can be used for this purpose. Moving parts, such as a bicycle chain, can be coated with oil or grease to both reduce friction and prevent contact with oxygen and moisture.



FIGURE 9.5.5 These food cans are made from steel that has been plated with tin to prevent them corroding.

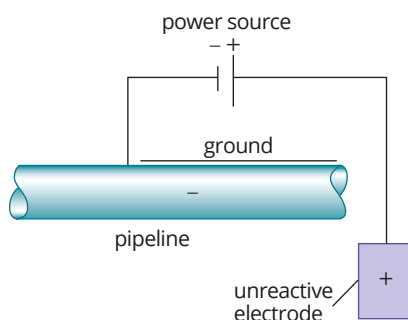


FIGURE 9.5.6 A pipeline carrying natural gas can be protected from corrosion if a direct current source is connected at intervals to give the pipe a negative charge.

Iron can also be protected by alloying with small quantities of metals such as chromium, nickel, manganese or molybdenum to produce stainless steel. The atoms of the metals used to make the **alloy** are all bonded into the metallic lattice. These metals oxidise slightly in air, but the oxide coating produced is continuous and unreactive. This oxide layer protects the metal from further oxidation.

Iron and steel can also be coated with thin layers of less reactive metals in a process known as **electroplating** (see Chapter 10). The ‘tin cans’ used to package food are made from steel plated with tin. Tin is a much less reactive metal than iron and does not corrode greatly in the atmosphere. In addition to the tin coating, cans used for food, such as the ones shown in Figure 9.5.5, have a plastic liner to prevent contact between the food and any metal oxides that may be present.

Electrochemical protection

Cathodic protection involves the use of a low-voltage, direct current (DC) power supply to give the iron being protected a negative charge. For corrosion to occur, the iron normally loses electrons (is oxidised). The act of making the iron negative pushes electrons towards the iron, thus reducing the chance of oxidation occurring. Instead, the iron becomes the site of the reduction reaction, and forms the cathode. This method, represented in Figure 9.5.6, is used to protect large-scale steel structures such as wharves and pipelines. A single DC source operating at 4.2 V and 2.5 A will protect many kilometres of pipeline.

Sacrificial protection also involves the iron acting as the cathode. A more easily oxidised metal, such as zinc, forms the anode and is ‘sacrificed’ in order to protect the iron from corrosion. The more reactive metal loses electrons and forms metal cations in preference to the iron.

Iron that has been coated in zinc is known as galvanised iron and is used widely for roofs and sheds, as shown in Figure 9.5.7a. Galvanised iron is an example of sacrificial protection. When the zinc coating is scratched, the iron is still protected because the zinc loses electrons more readily than the iron. The diagram in Figure 9.5.7b depicts this process. The zinc slowly corrodes but the iron is protected for years.

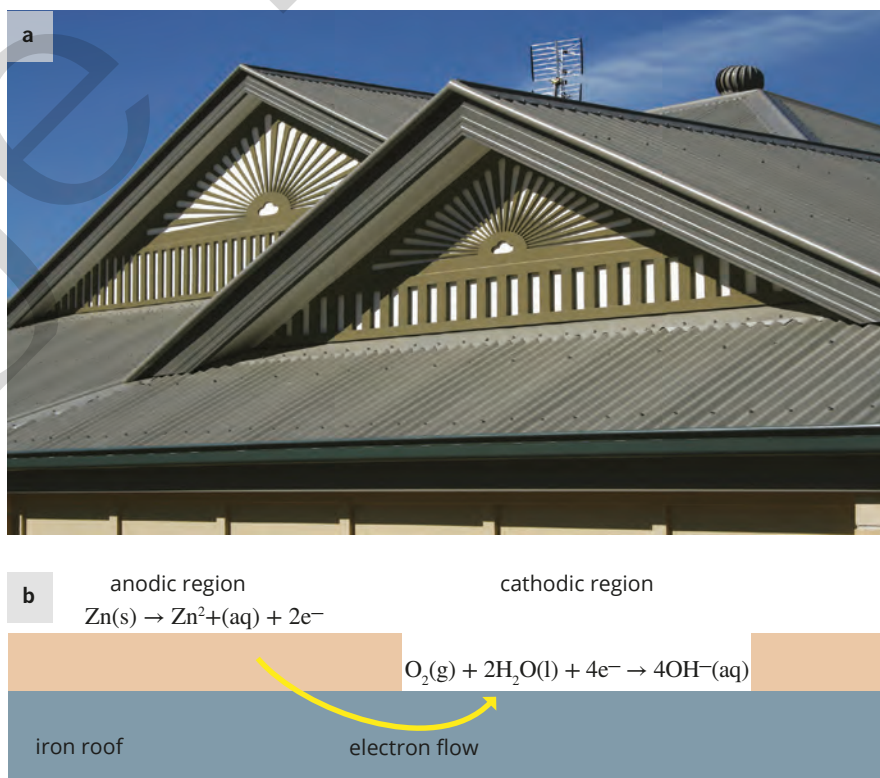


FIGURE 9.5.7 A galvanised iron roof is a common sight in Australia. The zinc coating is oxidised in preference to the iron, protecting the structural role of the iron.

Underground steel pipelines, bridge pillars and the steel hulls of ships can be protected by connecting them to blocks or plates of zinc, or other more reactive metals such as magnesium. Because these metals are more easily oxidised than iron, they lose electrons, which are transferred to the iron where reduction of oxygen and water occurs. The reactive metals, which are called **sacrificial anodes** are eventually consumed and must therefore be replaced, but this is less expensive than replacing the steel structures that are being protected (Figure 9.5.8).



FIGURE 9.5.8 These aluminium sacrificial anodes are attached to the underwater steel structures of offshore gas platforms to protect them against corrosion.

9.5 Review

SUMMARY

- Dry corrosion refers to the oxidation of a metal by oxygen gas.
- Wet corrosion involves both oxygen gas and water and can be considered as an electrochemical process.
- During the wet corrosion of iron, iron is oxidised to $\text{Fe}^{2+}(\text{aq})$ and oxygen gas is reduced to $\text{OH}^{-}(\text{aq})$. These form a precipitate of $\text{Fe}(\text{OH})_2(\text{s})$, which is converted to rust ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$).
- Protection measures against corrosion include surface coating, alloying, cathodic protection and the use of a more reactive metal as a sacrificial anode.

KEY QUESTIONS

- 1 Use equations to explain why the corrosion of iron is a redox process.
- 2 Explain why iron corrosion occurs more rapidly in coastal environments.
- 3 **a** Which one or more of the following metals could be used as a sacrificial anode to prevent the corrosion of iron: magnesium, zinc, lead, copper?
b Explain your answer to part **a** in terms of the reactivity series of metals.
- 4 Underwater steel pillars often corrode more rapidly just beneath the surface of the water than above. Suggest a reason for this.
- 5 Explain why it is common for steel nails to be coated with zinc rather than copper or tin.

Chapter review

KEY TERMS

accumulator
alkaline cell
alloy
anode
battery
biogas
cathode
cathodic protection
conjugate redox pair
direct corrosion
dry corrosion
electrochemical cell
electrochemical series
electrode

electrolyte
electrolytic cell
electromotive force
electroplating
external circuit
fuel cell
galvanic cell
galvanometer
half-cell
hydrogen economy
inert electrode
internal circuit
lead–acid battery
lithium-ion cell

nickel–metal hydride cell
non-rechargeable cell
oxidant
oxidising agent
potential difference
primary cell
rechargeable cell
redox reaction
reducing agent
reductant
sacrificial anode
sacrificial protection
salt bridge
secondary cell

09

spontaneous reaction
standard conditions
standard electrode potential
standard hydrogen half-cell
standard reduction potential
volt
voltaic cell
voltmeter
wet corrosion

Galvanic cells

- Which one of the following statements best describes the role of the salt bridge in a galvanic cell?
 - It allows positive charges to accumulate in one half-cell and negative charges to accumulate in the other.
 - It provides a pathway for electrons to move between the half-cells.
 - It allows reactants from one half-cell to mix with reactants from the other half-cell.
 - It allows movement of ions to balance charges formed at the electrodes.
- Which one of the following materials would be least suitable for use as an electrode in a $\text{Cl}_2(\text{g})/\text{Cl}^-(\text{aq})$ half-cell?
 - Iron
 - Platinum
 - Graphite
 - Gold
- Explain the difference between:
 - oxidising agent and reducing agent
 - anode and cathode
 - conjugate redox pair and conjugate acid–base pair
 - external circuit and internal circuit.
- The overall reaction for a galvanic cell constructed from the $\text{Cl}_2(\text{g})/\text{Cl}^-(\text{aq})$ and $\text{Pb}^{2+}(\text{aq})/\text{Pb}(\text{s})$ half-cells is:
$$\text{Cl}_2(\text{g}) + \text{Pb}(\text{s}) \rightarrow 2\text{Cl}^-(\text{aq}) + \text{Pb}^{2+}(\text{aq})$$
A platinum electrode is used in the $\text{Cl}_2(\text{g})/\text{Cl}^-(\text{aq})$ half-cell.
 - Draw a diagram of the galvanic cell and on your diagram show:
 - the direction of electron flow in the external circuit
 - a half-equation for the reaction at each electrode
 - which electrode is the anode
 - which electrode is positive
 - which way cations flow in the salt bridge.
 - Write the galvanic cell in shorthand cell notation.
- Two half-cells are set up. One contains a solution of magnesium nitrate with a strip of magnesium as the electrode. The other contains lead nitrate with a strip of lead as the electrode. The solutions in the two half-cells are connected by a piece of filter paper soaked in potassium nitrate solution. When the electrodes are connected by wires to a galvanometer, the magnesium electrode is shown to be negatively charged.
 - Sketch the galvanic cell described. Label the positive and negative electrodes. Mark the direction of the electron flow.
 - Write the half-equations for the reactions that occur in each half-cell and an equation for the overall reaction.
 - Label the anode and cathode.
 - Indicate the direction in which ions in the salt bridge migrate.

The electrochemical series

- Show that under standard conditions, according to the electrochemical series, the Daniell cell (Figure 9.1.4, page 213) should have a cell potential difference of 1.10 V.

- 7 The two galvanic cells shown in Figure 9.6.1 were constructed under standard conditions.

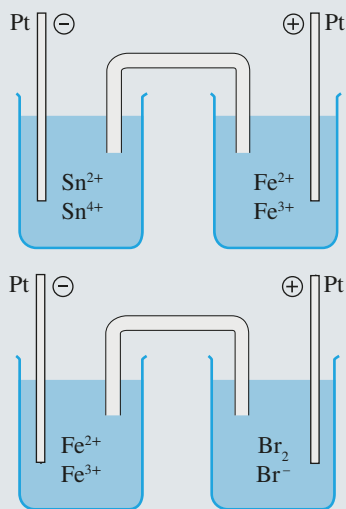


FIGURE 9.6.1 Two galvanic cells

On the basis of the electrode polarities, determine the order of reducing agent strength from strongest to weakest.

- 8 Consider the four galvanic cells made from half-cells as listed below. Use the electrochemical series to rank the galvanic cells in order of the maximum voltage they could generate under standard conditions.
- $\text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s})$ and $\text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq})$
 - $\text{Ni}^{2+}(\text{aq})/\text{Ni}(\text{s})$ and $\text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s})$
 - $\text{Ni}^{2+}(\text{aq})/\text{Ni}(\text{s})$ and $\text{Br}_2(\text{l})/\text{Br}^{-}(\text{aq})$
 - $\text{Ni}^{2+}(\text{aq})/\text{Ni}(\text{s})$ and $\text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq})$
- 9 Each of these pairs of half-cells combines to form a galvanic cell.
- a $\text{Ag}^{+}(\text{aq})/\text{Ag}(\text{s})$ and $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$
 - b $\text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s})$ and $\text{Pb}^{2+}(\text{aq})/\text{Pb}(\text{s})$
 - c $\text{Ni}^{2+}(\text{aq})/\text{Ni}(\text{s})$ and $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$

Draw a diagram of each galvanic cell and on your diagrams show:

- the direction of electron flow in the external circuit
- a half-equation for the reaction at each electrode
- an equation for the overall reaction in the galvanic cell
- which electrode is the anode
- which electrode is positive
- which way negative ions flow in the salt bridge.

- 10 Four half-cells $\text{A}^{2+}(\text{aq})/\text{A}(\text{s})$, $\text{B}^{2+}(\text{aq})/\text{B}(\text{s})$, $\text{C}^{2+}(\text{aq})/\text{C}(\text{s})$ and $\text{D}^{2+}(\text{aq})/\text{D}(\text{s})$ are used to make the cells shown below.

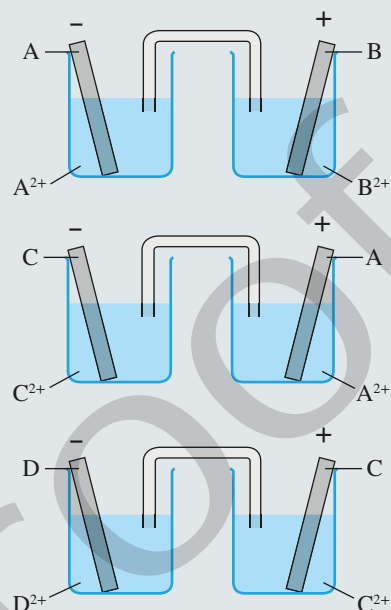
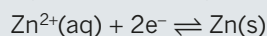
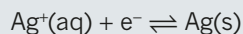
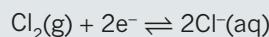


FIGURE 9.6.2 Four half-cells

Rank the half-cells in order of their reduction half-cell potentials, from highest to lowest.

Predicting direct redox reactions

- 11 The following equations appear in the order shown in the electrochemical series:



- i Predict whether a redox reaction would occur in the following mixtures. Assume concentrations of 1 mol L^{-1} and gas pressures of 1 bar. For mixtures where you predict a reaction will occur, write:
 - ii separate half-equations for the oxidation and reduction reactions
 - iii an overall equation.
- a $\text{Cl}_2(\text{g})$ and $\text{Zn}(\text{s})$
 - b $\text{Ag}^{+}(\text{aq})$ and $\text{Ag}(\text{s})$
 - c $\text{Ag}^{+}(\text{aq})$ and $\text{Zn}(\text{s})$
 - d $\text{Zn}^{2+}(\text{aq})$ and $\text{Cl}^{-}(\text{aq})$

- 12** Use the electrochemical series to predict whether a reaction will occur in each of the following situations. Write an equation for each reaction that you predict will occur.
- Copper(II) sulfate solution is stored in an aluminium container.
 - Sodium chloride solution is stored in a copper container.
 - Silver nitrate solution is stored in a zinc container.
 - An iron nail is placed in 1 mol L^{-1} hydrochloric acid solution.
 - A plumber uses hydrochloric acid to clean copper pipes.
- 13** The following equations form part of the electrochemical series. They are ranked in the order shown.
- $$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$$
- $$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s})$$
- $$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$$
- $$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$$
- $$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg}(\text{s})$$
- Which species is the strongest oxidising agent and which species is the weakest oxidising agent?
 - Which species is the strongest reducing agent and which species is the weakest reducing agent?
 - Lead rods are placed in solutions of silver nitrate, iron(II) sulfate and magnesium chloride. In which solutions would you expect to see a coating of another metal form on the lead rod? Explain.
 - Which of the metals silver, zinc or magnesium might be coated with lead when immersed in a solution of lead(II) nitrate?
- 14** Use the electrochemical series to determine whether:
- elemental iodine is an oxidising agent or a reducing agent
 - calcium metal is a strong or weak reducing agent
 - nickel is a better reducing agent than silver
 - $\text{Cu}^{2+}(\text{aq})$ is a better oxidising agent than $\text{Ag}^+(\text{aq})$
 - $\text{Fe}^{2+}(\text{aq})$ can act as an oxidising agent and a reducing agent.
- 15**
- Use the electrochemical series to predict what might be expected to occur if hydrogen gas were bubbled through a solution containing Fe^{3+} ions.
 - Write an equation for the predicted reaction.
 - When the reactants were mixed in an experiment, no reaction was observed. Suggest possible reasons for this.

Everyday sources of power

- 16** Match the following terms with their correct definition.

Term	Definition
Galvanic cell	A cell in which reactants are supplied continuously
Primary cell	A device that converts chemical energy into electrical energy
Secondary cell	A non-rechargeable galvanic cell
Fuel cell	A rechargeable galvanic cell

- 17** Explain the difference between:
- anode and cathode
 - cell and battery
 - discharge and recharge.
- 18** Label the diagram of a hydrogen–oxygen fuel cell shown in Figure 9.6.3.

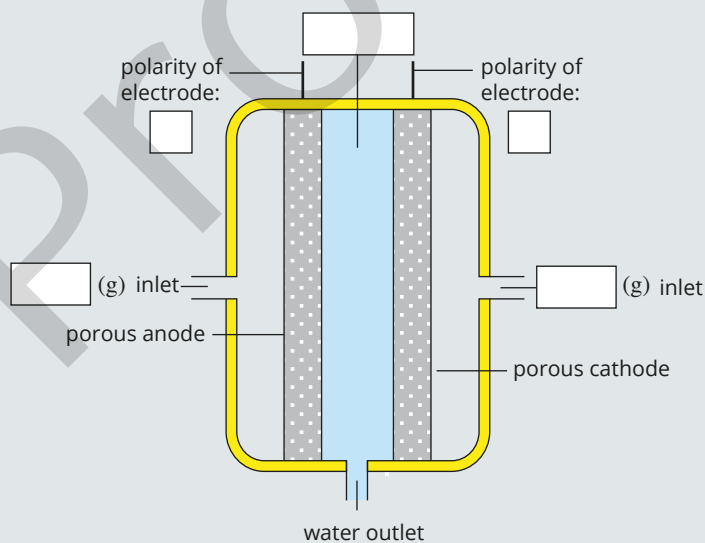


FIGURE 9.6.3 Hydrogen–oxygen fuel cell

- 19** Which one of the following reactions might be used as the basis for an experimental fuel cell?
- $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$
 - $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$
 - $\text{HCl}(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$
 - $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{CO}_3(\text{aq})$
- 20** Decide whether the following statements apply to fuel cells, primary cells or secondary cells. Some statements apply to all types of cells.
- They convert chemical to electrical energy.
 - Oxidation occurs at the anode and reduction occurs at the cathode.
 - The anode is the negative electrode as the cell generates electricity.
 - They are recharged by connecting to a power supply.
 - Electrode reactions occur in separate compartments.
 - Chemical energy is stored within the cell.
 - The reactant is supplied constantly.

- 21 Mains electricity costs about 5 cents per MJ of energy, or less, depending on the tariff. The cost of the same amount of electrical energy produced by a cell is far more—about \$1300 for a dry cell and even more for a button cell. Why are people prepared to use cells and pay such relatively high prices for electricity?

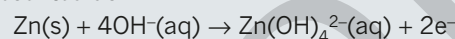
Corrosion

- 22 Which one of the following factors does not increase the rate of corrosion of a metal object?
- The presence of water with dissolved oxygen
 - The presence of impurities, such as salt, dissolved in water
 - The presence of acidic pollutants dissolved in water
 - The presence of a coating of paint over the surface of the metal object
- 23 Consider the following products that are made during the wet corrosion of iron. List them in the correct order in which they are made: $\text{Fe}(\text{OH})_3(\text{s})$, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{s})$, $\text{Fe}(\text{OH})_2(\text{s})$, $\text{Fe}^{2+}(\text{aq})$ and $\text{OH}^-(\text{aq})$.
- 24 Why is it usually not necessary to protect structures made of copper from corrosion?
- 25 Steel garden furniture rusts much more readily near the seaside than inland. Explain why.

Connecting the main ideas

- 26 Fill in the blanks in the following passage about galvanic cells.
- The redox reaction occurring in a galvanic cell takes place in two _____. The electrode at which oxidation occurs is called the _____, whereas the other electrode where reduction occurs is the _____. The polarity of the anode is _____ and the polarity of the cathode is _____.
- Galvanic cells can be classified as either primary cells, which _____ be recharged, or secondary cells, which _____ be recharged.
- 27 A student was told that the redox pair $\text{Mn}^{2+}(\text{aq})/\text{Mn}(\text{s})$ is lower in the electrochemical series than the $\text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s})$ pair and higher than $\text{Al}^{3+}(\text{aq})/\text{Al}(\text{s})$. Explain how the student could experimentally determine the relative positions of the three pairs in the series.
- 28 Account for the following observations.
- Bromine reacts with iodide ions in solution but does not react with chloride ions.
 - Hydrogen peroxide (H_2O_2) solution can spontaneously decompose to form water and oxygen.
 - Tin metal is added to solutions of tin(II) chloride to prevent oxidation of the tin(II) ions by oxygen in air.
 - Blocks of zinc are attached to the iron hulls of ships to reduce corrosion.

- 29 A student working in the laboratory spilled an iodine solution over the bench, causing a dark brown stain to form. Suggest how the student could remove the iodine stain.
- 30 What are the limitations that need to be considered when using the electrochemical series to predict whether or not a certain reaction will occur?
- 31 Many of the 'alkaline cells' on the market contain zinc electrodes in contact with an electrolyte containing hydroxide ions. The half-cell reaction might be represented as:



To investigate if the standard electrode potential (E°) of these half-cells is the same as that of a half-cell reaction using a zinc electrode in contact with a zinc nitrate electrolyte (for which the electrode reaction would be $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$) a student was provided with the two half-cells shown in Figure 9.6.4, as well as a $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ half-cell.

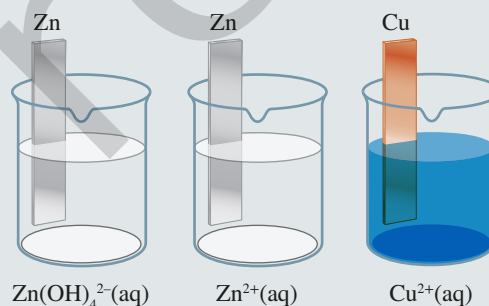


FIGURE 9.6.4 Two zinc electrode half-cells and a $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ half-cell

- Write a net equation for the reaction in a galvanic cell in which the 'alkaline zinc half-cell' is connected to the Cu^{2+}/Cu half-cell.
 - Carefully explain how the student could use the half-cells that were provided to determine whether the two different half-cells containing zinc had the same E° value. Include fully labelled diagrams with your answer and explain how the results could be interpreted.
- 32 Consider the similarities and differences between a primary cell and a fuel cell.
- List the design features that the two types of cells have in common.
 - List the design features that are different in the two types of cells.
- 33 'Hydrogen–oxygen fuel cells are the energy source of the future.' Discuss the advantages and disadvantages of an energy supply based on these fuel cells.

UNIT 3 • EQUILIBRIUM, ACIDS AND BASES, AND REDOX REACTIONS

REVIEW QUESTIONS

Section 1: Multiple choice

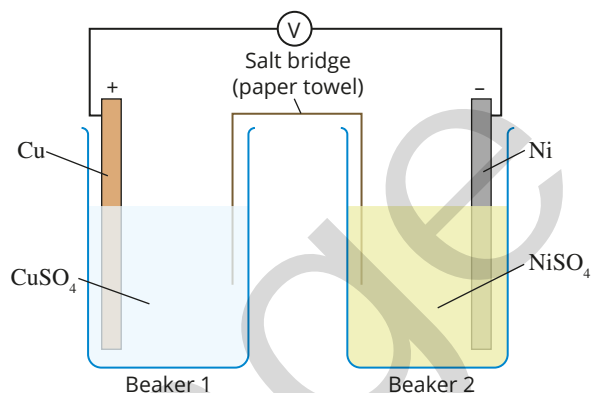
1 Which of the following lists species arranged with the nitrogen atoms in order of increasing oxidation number?

- A NH_4^+ , N_2 , NO , NO_3^-
- B NO_3^- , NO , NH_3 , N_2
- C NO_2 , N_2 , NO , HNO_3
- D NO_3^- , NO , N_2 , NH_3

2 Use the electrochemical series to determine which one of the following would not be expected to occur to an appreciable extent.

- A $2\text{H}^+(\text{aq}) + \text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
- B $2\text{Ag}^+(\text{aq}) + \text{Ni}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \text{Ni}^{2+}(\text{aq})$
- C $\text{Br}_2(\text{aq}) + 2\text{Fe}^{2+}(\text{aq}) \rightarrow 2\text{Br}^-(\text{aq}) + 2\text{Fe}^{3+}(\text{aq})$
- D $2\text{I}^-(\text{aq}) + \text{Pb}^{2+}(\text{aq}) \rightarrow \text{I}_2(\text{s}) + \text{Pb}(\text{s})$

3 An electrochemical cell was made by dipping a copper rod into a solution of $1 \text{ mol L}^{-1} \text{ CuSO}_4$ in one beaker and dipping a nickel rod into a solution of $1 \text{ mol L}^{-1} \text{ NiSO}_4$ in another beaker. The metals were connected with wire and the two solutions were connected by a piece of paper towel that had been soaked in a potassium nitrate solution. The cell is shown in the following diagram.



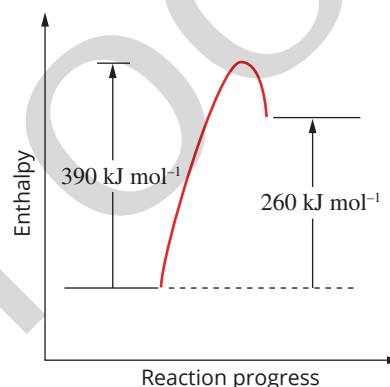
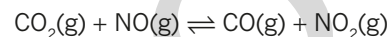
The solution in beaker 1 was initially coloured blue, owing to the presence of Cu^{2+} ions. The solution in beaker 2 was initially coloured green because of the presence of Ni^{2+} ions. Which of the following changes might it be possible to detect after the galvanic cell has been discharging for a period of time?

- A The green colour in beaker 2 has faded and the mass of the copper electrode has increased.
- B The blue colour in beaker 1 has faded and the mass of the nickel electrode has increased.
- C The green colour in beaker 2 has faded and the mass of the copper electrode has decreased.
- D The blue colour in beaker 1 has faded and the mass of the nickel electrode has decreased.

4 Which of the following requires involvement of a reversible chemical reaction?

- A Combustion of a fuel to produce heat for cooking
- B An electric car powered by a dry cell
- C The rechargeable battery in a mobile phone
- D The setting of a two-part epoxy glue after the parts are mixed

5 The energy profile diagram shown below is for the reaction:



Which of the following shows the activation energy and ΔH of the reverse reaction?

	Activation energy of reverse reaction (kJ mol^{-1})	ΔH of reverse reaction (kJ mol^{-1})
A	-390	+260
B	+130	-260
C	+130	+260
D	-390	-260

6 A student conducted an acid–base volumetric analysis experiment. A 20.0 mL aliquot of a 0.10 mol L^{-1} solution of hydrochloric acid was pipetted into a flask. A 0.10 mol L^{-1} solution of potassium hydroxide was added from a burette. A titre of 19.5 mL was obtained, not the expected 20.0 mL value. Which of the following procedures could be a reason for the low titre?

- A The student accidentally used a 25.0 mL pipette.
- B The 20.0 mL pipette was rinsed with water immediately prior to delivering the aliquot.
- C The conical flask was rinsed with water prior to the titration.
- D The burette was rinsed with water immediately prior to adding the potassium hydroxide solution.

- 7 Which of the following statements about a catalyst is not true?
- A A catalyst is not consumed in the course of a reaction.
 - B A catalyst alters the reaction pathway between reactants and products.
 - C A catalyst reduces the energy released or absorbed by a reaction.
 - D The proportion of molecules with sufficient energy to react is increased by a catalyst.

- 8 In a sealed vessel, nitrogen monoxide, oxygen and nitrogen dioxide form the following equilibrium:
- $$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) \quad \Delta H = -114 \text{ kJ mol}^{-1}$$
- Which one of the following sets of conditions is likely to lead to the highest yield of nitrogen dioxide gas?

- A 200°C and 100 kPa pressure
- B 200°C and 200 kPa pressure
- C 300°C and 100 kPa pressure
- D 300°C and 200 kPa pressure

- 9 The reaction between nitrogen monoxide and ozone is:
- $$\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightleftharpoons \text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \quad K = 6 \times 10^{34} \text{ at } 25^\circ\text{C}$$
- Equal amounts of NO and O₃ are used. Which of the following statements cannot be inferred from the magnitude of the equilibrium constant?

- A At equilibrium, $[\text{NO}_2][\text{O}_2] > [\text{NO}][\text{O}_3]$.
- B The equilibrium of the reaction lies to the right.
- C The reaction has a low activation energy.
- D Very little ozone will remain at equilibrium.

- 10 The endpoint of an acid-base titration is the point at which:
- A the reactants have been mixed in the mole ratios given in the balanced equation for the reaction.
 - B the pH of the solution in the titration flask is 7.
 - C equal volumes of reactant solutions have been added.
 - D the indicator changes colour.

- 11 In an experiment, the following standard half cells were set up.

- I Mn^{2+}/Mn
- II Ni^{2+}/Ni
- III Mg^{2+}/Mg
- IV Fe^{2+}/Fe

Which combination of half-cells will produce the lowest cell voltage?

- A I and II
- B III and IV
- C I and III
- D II and III

- 12 The following table shows the characteristics of the indicator methyl red.

Low pH colour	Transition pH range	High pH colour
red	4.4–6.2	yellow

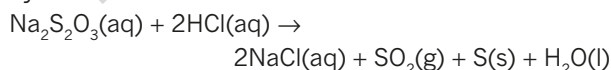
During the titration of a 0.1 mol L⁻¹ solution of the weak base ammonia using a standardised hydrochloric acid solution, the most appropriate determination of the endpoint of the titration would be a colour change for methyl red from:

- A red to yellow occurring at a pH of 7.
- B yellow to red occurring at a pH of 7.
- C yellow to red occurring at a pH above 7.
- D yellow to red occurring at a pH below 7.

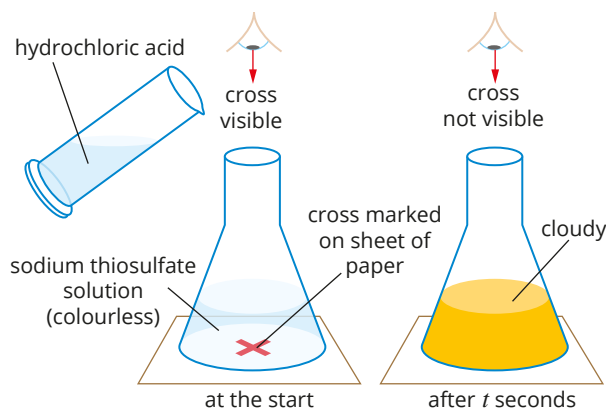
Section 2: Short answer

- 1 Two experiments were conducted to investigate the rate of reactions for both aqueous and gaseous reaction mixtures.

- a A student investigated the factors affecting the rate of reaction between a solution of sodium thiosulfate and hydrochloric acid:



The reaction was carried out in a conical flask placed on top of a piece of white paper with a dark cross marked on it. The rate of reaction was determined by measuring the time taken for the cross to be masked by the suspension of sulfur formed during the reaction, as shown.

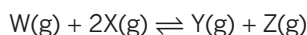


UNIT 3 • REVIEW

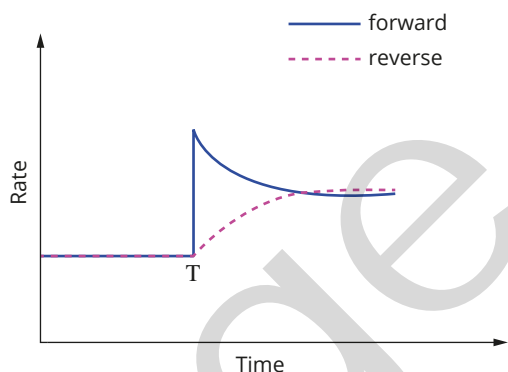
The rate was determined for different concentrations of sodium thiosulfate and for different temperatures. The volume of each solution and the concentration of hydrochloric acid were kept constant. The results are summarised in the following table.

Experiment number	Concentration of $\text{Na}_2\text{S}_2\text{O}_3$ (aq) (mol L^{-1})	Temperature ($^{\circ}\text{C}$)	Time taken for the cross to be masked (s)
1	0.1	20	36
2	0.2	20	20
3	0.1	25	28

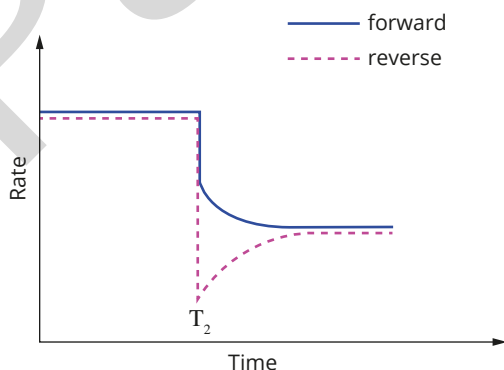
- Explain, in terms of collision theory, why the rate in experiment 2 is higher than the rate in experiment 1.
 - Explain, in terms of collision theory, why the rate in experiment 3 is higher than the rate in experiment 1.
- b** In the second investigation a readily reversible gas-phase reaction was used:



The following graph shows the changes to the rates of the forward and reverse reactions when some additional reactant, W, is added to an equilibrium mixture of these gases at time T.

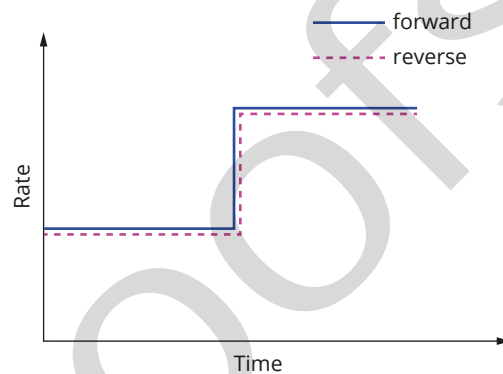


- Explain how this graph shows that the mixture was at equilibrium before time T.
 - Use collision theory to account for the change in the rate of the reverse reaction from time T.
- The following graph shows the rate changes after lowering the temperature at time T_2 .



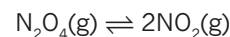
- Considering the period during which the rates are unequal, in which direction does the equilibrium shift?
- Is the reaction exothermic or endothermic? Explain.

The following graph shows the rate change when a change was made to the system at time T_3 .

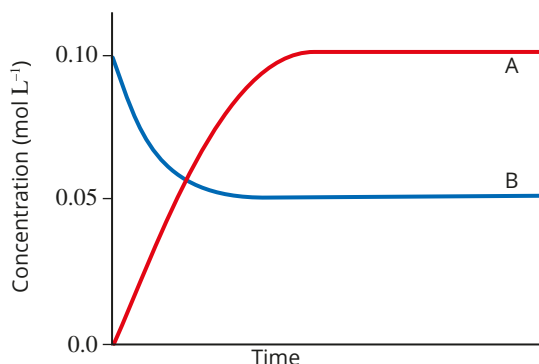


- Suggest what change was made to the system to produce the rate graph shown.

- 2** The gases dinitrogen tetroxide, N_2O_4 , and nitrogen(IV) oxide, NO_2 , coexist according to the following equilibrium reaction:



A concentration–time graph for the system establishing equilibrium is shown below.



- Identify A and B assuming there was no N_2O_4 present initially.
- Write an expression for the equilibrium constant of the decomposition of N_2O_4 .
- On the graph, sketch the line showing the effect on A if a catalyst had been present in the mixture from the beginning.
- Use your knowledge of Le Châtelier's principle to predict the effect (decrease, increase or no change) of the change (column 1) on the designated quantity (column 2). Assume that the change listed is the only one taking place (e.g. if N_2O_4 is added, the volume and the temperature are kept constant).

Change	Quantity	Increase/decrease/ no change
i Double the volume	Amount of NO_2	
ii Double the volume	Concentration of NO_2	
iii Add an inert gas at constant volume	Amount of N_2O_4	

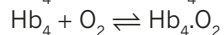
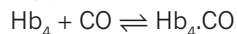
- 3 a** Lithium metal is produced commercially by electrolysis of a molten mixture of lithium chloride and potassium chloride.
- Write the half-equation for the electrode reaction occurring at the anode
 - Write the half-equation for the electrode reaction occurring at the cathode.
 - Why is it not possible to produce lithium metal by the electrolysis of an aqueous solution of lithium chloride?
 - Suggest why a mixture of lithium chloride and potassium chloride is used, rather than pure lithium chloride, in this electrolytic process.
- b** Suggest three properties of graphite that account for its frequent use as an electrode material in commercial electrolytic cells.
- c** Steel cathodes are often used in commercial electrolytic cells but never steel anodes. Account for this.
- 4 a** List two structural features (components) that galvanic cells and electrolytic cells both possess.
- b** Compare the energy transformations occurring in a galvanic cell with those occurring in an electrolytic cell.
- c** Explain why the negative electrode of a galvanic cell is the site of oxidation, whereas the negative electrode of an electrolytic cell is the site of reduction.
- d** Explain why a galvanic cell is always constructed to keep its reacting oxidising agent and reducing agent apart, while in an electrolytic cell they are usually combined in the same electrolyte mixture and instead steps are taken to keep the cell products apart.
- 5** Hydrogen sulfide (H_2S) can act as a weak acid and as a reducing agent in aqueous solution.
- Write an equation for the first ionisation of hydrogen sulfide in water.
 - Write an expression for the equilibrium constant (K) for hydrogen sulfide ionisation in terms of the concentration of the chemical species present.
 - 1.7 g of hydrogen sulfide will dissolve in 500.0 mL of water at room temperature to form a saturated solution. Calculate the concentration of this solution.
 - Addition of solid sodium hydrogensulfide (NaHS) to this saturated solution will form a buffer solution.
 - What is a buffer solution?
 - Using Le Châtelier's principle, explain what happens in this buffer solution when a small amount of $\text{HCl}(\text{aq})$ is added.
- d** Write a balanced ionic equation to show $\text{H}_2\text{S}(\text{aq})$ acting as a reducing agent in reaction with a silver nitrate solution.
- 6 a** An old metal key composed mainly of iron, but showing some signs of forming an iron oxide (Fe_2O_3) coating, was placed into a dilute sulfuric acid solution. The key reacted slowly, removing the oxide layer, and then releasing hydrogen gas.
- Write a balanced equation for the reaction between the iron and sulfuric acid.
 - Show that this reaction is a redox reaction.
 - Write a balanced equation for the reaction between the iron oxide and sulfuric acid.
 - Show that this reaction is an acid-base reaction.
- b** A student wishes to electroplate copper metal onto the key, after first cleaning the surface of the metal.
- Draw a diagram of the cell needed to achieve this aim, using the key as one electrode and a strip of copper metal as the other.
 - Indicate on the diagram the polarity of the power source (positive or negative) to which the key should be attached.
 - Which electrode (the cathode or the anode) is the key?
 - Show why the concentration of Cu^{2+} ions in the electrolyte does not change.
 - If the copper electrode was replaced with a graphite electrode, how would the pH near the electrode change as the electrolysis continued?

Section 3: Extended answer

- 1** Methanol can be used as a fuel for some racing cars, and can be used to generate energy in a direct methanol fuel cell (DMFC). The synthesis of methanol from methane involves two reversible reactions.
- A reaction of methane with steam to yield carbon monoxide and hydrogen
 - An exothermic reaction between carbon monoxide and hydrogen to produce methanol
- a** Write equations for the two reactions (I and II) that are described.
- b** The reaction of carbon monoxide with hydrogen (reaction II) is performed in a reactor at about 250°C and 100 times atmospheric pressure. Copper, zinc oxide and alumina are also present.
- What is the likely function of the copper, zinc oxide and alumina in the reactor?
 - How would the yield of methanol be affected if the reaction were performed at a higher temperature?
 - State two advantages of using such a high pressure in the reactor.

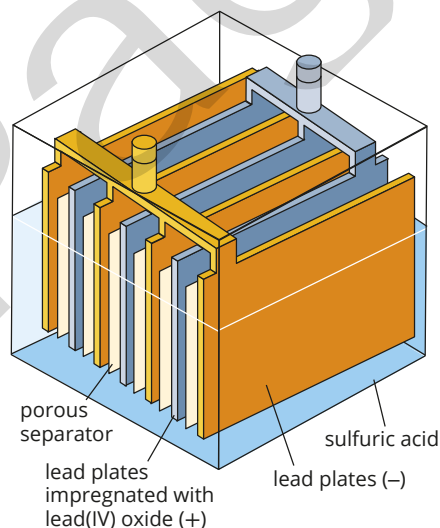
UNIT 3 • REVIEW

- c Any process involving carbon monoxide presents hazards because of its toxicity, which arises because of its ability to bind very strongly to haemoglobin (represented as Hb_4) in the blood, in competition with oxygen. The simplified equations are:



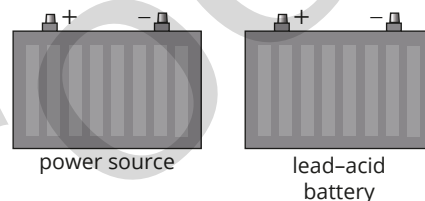
Referring to these competing equilibria, explain why exposure to carbon monoxide leads to decreased levels of oxyhaemoglobin (Hb_4O_2) in the blood.

- d Draw an energy profile for reaction of methanol as a fuel. Include the following labels on your profile: reactants, products, ΔH , activation energy
- e The equation for the reaction in the DMFC is the same as that for the direct combustion of methanol with liquid water as a product. The fuel cell has an acidic electrolyte.
- Write a balanced equation for the combustion of methanol to produce carbon dioxide and water.
 - Write the half-equation for the reaction occurring at the anode
 - Write the half-equation for the reaction occurring at the cathode.
- iv Fuel cells provide an alternative method, often more efficient than direct combustion, of extracting energy from the reaction between a fuel and oxygen. Compare the energy transformation occurring in a fuel cell with that occurring in a direct combustion reaction.
- v Fuel cells share a number of similarities to galvanic cells, but have several differences. State one similarity and one difference between a fuel cell and a galvanic cell.
- f Fuel cells may provide an energy source suitable for use in electric powered vehicles. Another possible energy source is the lead-acid battery, made up of six lead-acid cells connected in series. A simplified diagram of the lead-acid battery is shown below.



- Write an equation for the overall cell reaction when electrical energy is being produced.
 - Calculate the voltage of the cell using the E° values provided in the Data Book.
 - Suggest a reason why the actual voltage of the cell could be different to the voltage calculated from the E° values.
- iv What type of reaction (oxidation or reduction) occurs at the negative electrode when the cell is discharging?
- v To recharge the lead-acid battery, an external power supply must be attached to the electrodes.

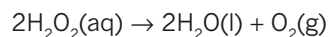
On the diagram, draw lines to represent wires showing the correct connections to recharge the lead-acid battery.



- 2 a Ethanoic acid (CH_3COOH) is a monoprotic weak acid found in vinegar.
- Explain the meaning of the term 'weak acid'.
 - Write an expression for the equilibrium constant (K) for ethanoic acid ionising in water in terms of the concentration of the chemical species present.
- b In a volumetric analysis to determine the concentration of an ethanoic acid solution, 10.0 mL of the acid was diluted to a total volume of 250.0 mL in a standard flask. 20.00 mL aliquots of this diluted acid solution were separately titrated with a standardised 0.100 mol L⁻¹ solution of sodium hydroxide. The average volume to reach the endpoint was 18.5 mL.
- Methyl orange indicator was used in the titration. What is the purpose of the indicator?
 - Write a balanced equation for the titration reaction.
 - Calculate the concentration of the undiluted ethanoic acid.
 - Calculate the pH of the 0.100 mol L⁻¹ sodium hydroxide solution.
- c In a separate titration experiment the 0.100 mol L⁻¹ sodium hydroxide solution was used to titrate 25.0 mL of a 0.10 mol L⁻¹ hydrochloric acid solution.
- State the volume of sodium hydroxide needed for complete reaction.
 - State the pH value at the start of the titration
 - State the pH value at the equivalence point
 - The experiment in was repeated using a 25.0 mL sample of 0.10 mol L⁻¹ ethanoic acid in the conical flask instead of the hydrochloric acid. For this titration would the value of the pH at the equivalence point be equal to, greater than, or less

than the value for the titration using hydrochloric acid? Explain your choice.

- d** Like ethanoic acid, hydrogen peroxide (H_2O_2) is a weak acid. In addition to being an acid, hydrogen peroxide is both an oxidising agent and a reducing agent. Hydrogen peroxide reacts with itself according to the equation:



- i** Write an equation to show the first ionisation of hydrogen peroxide when it acts as an acid.
- ii** While hydrogen peroxide does undergo this decomposition reaction, bottles of hydrogen peroxide can be kept in a dark bottle on the bathroom shelf for an extended period of time. Hydrogen peroxide solutions are also kept in the refrigerator. Explain why hydrogen peroxide solutions can be stored, and why they are often refrigerated.
- e** Like hydrogen peroxide, water can act as an acid, an oxidising agent and a reducing agent. Pure water has

a very low, but measurable, electrical conductivity. At 25°C the pH of pure water is 7. The ionic product of water (K_w) varies with temperature as shown in the following table.

Temperature ($^\circ\text{C}$)	5	15	35	55
K_w	1.85×10^{-15}	4.51×10^{-15}	2.09×10^{-14}	7.29×10^{-14}

- i** Why does pure water conduct electricity, and why is this conductivity extremely low? Include a balanced chemical equation in your response.
- ii** What is the pH of pure water at 5°C ?
- iii** Calculate the concentration of the hydroxide ion in water at 35° .
- iv** How is water acting in the reaction represented by the equation shown below? Select your answer from the terms: acid, base, reducing agent, oxidising agent.

