Galvanic cells convert chemical energy to electrical energy from spontaneous chemical reactions. The reverse process occurs in electrolytic cells. During electrolysis, an electrical current is passed through an electrolyte causing a chemical reaction that would not otherwise occur. Electrolysis reactions form the basis of a number of important industrial processes.

YOU WILL EXAMINE:
- energy transformations in electrolytic cells
- the differences between galvanic and electrolytic cells
- how to use the electrochemical series to predict the products of redox reactions in electrolytic cells and the limitations of these predictions
- some examples of commercial electrolysis
- rechargeable batteries
- some of the factors that affect battery life
- how to apply Faraday’s laws to calculate quantities in redox reactions.

In the south of France lies the village of Les Baux en Provence. It was near here, in 1821, that the ore bauxite was discovered. This is the ore from which aluminium is produced. It is hard to reconcile the quaintness of this village with the huge industry that has grown from this discovery. Here in Australia we have huge deposits of this ore, making us the largest producer in the world.

Aluminium is obtained by the process of electrolysis. This uses electricity to bring about non-spontaneous redox reactions. The development of electrolysis on a large scale was not possible until large supplies of cheap electricity became available.

Modern electrolysis is involved in the production of many other important chemicals, as well as numerous everyday processes such as electroplating jewellery, protecting metal and recharging batteries.
Metals through the ages

The extraction of metals such as aluminium, magnesium, calcium and sodium was not achieved until the nineteenth century. Not until electrolysis was discovered could these elements be obtained from their compounds in significant amounts.

We have already seen how a spontaneous chemical reaction can be used to generate a flow of electrons (an electric current). In this chapter, you will see how an electric current can be used to make a non-spontaneous redox reaction occur.

Electrolysis — the process

In an electrochemical cell or galvanic cell, a spontaneous chemical reaction produces an electric current. In an electrolytic cell, the reverse process takes place. The passage of an electric current through an electrolytic solution causes a chemical reaction. This process is known as electrolysis.

In galvanic cells, chemical reactions can be used to generate a flow of electrons (an electric current). If a zinc rod is placed in copper(II) sulfate solution, a coating of copper appears on the zinc rod. This may be explained by considering the standard electrode potentials of each half-equation:

\[ \text{Cu}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cu}(s) \quad E^* = +0.34 \text{ V} \]
\[ \text{Zn}^{2+}(aq) + 2e^- \rightleftharpoons \text{Zn}(s) \quad E^* = -0.76 \text{ V} \]
Since the $E^\circ$ value for the $\text{Cu}^{2+}/\text{Cu}$ redox pair is greater than the $E^\circ$ value for the $\text{Zn}^{2+}/\text{Zn}$ redox pair, Cu$^{2+}$ ions react spontaneously with zinc metal. A galvanic cell constructed from these two half-cells would produce electrical energy. The overall equation for such a galvanic cell would be:

$$\text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq) + \text{energy}$$

However, if a copper rod is placed in a zinc sulfate solution, no reaction occurs. Since this reaction is the reverse of the one that produces energy, energy must be supplied for the reaction to occur:

$$\text{Cu}(s) + \text{Zn}^{2+}(aq) + \text{energy} \rightarrow \text{Cu}^{2+}(aq) + \text{Zn}(s)$$

**Electrolytic cells**

The chemical reaction that occurs when electricity passes through a molten ionic compound or through an electrolyte solution is called electrolysis. Solutes that form solutions that can conduct electricity are called **electrolytes**. An electrolyte solution conducts electricity. Positive ions gain electrons at the cathode and negative ions lose electrons at the anode. This transfer of electrons has the same effect as a flow of electrons, and the solution conducts electricity. The apparatus in which electrolysis occurs is called an **electrolytic cell**.

An electrolytic cell has three essential features:

1. an electrolyte solution that contains free-moving ions. These ions can donate or accept electrons, allowing electrons to flow through the external circuit.
2. two electrodes at which the electrolysis reactions occur
3. an external source of electrons, such as a battery or power pack. This electron flow is in one direction only and is termed DC (direct current).

The electrode to which electrons flow from the external power source is the negative electrode and is called the **cathode**, since reduction occurs there. The electrode from which electrons are withdrawn by the power source is the positive electrode and is called the **anode**, since oxidation occurs there. Cations are attracted to the cathode, while anions are attracted to the anode. The cations gain electrons from the cathode and the anions give up electrons to the anode.
Comparing galvanic and electrolytic cells

Consider the following redox half-equations:

\[ \text{Cu}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cu}(s) \quad E^* = +0.34 \text{ V} \]
\[ \text{Zn}^{2+}(aq) + 2e^- \rightleftharpoons \text{Zn}(s) \quad E^* = -0.76 \text{ V} \]

Electrical energy can be obtained from the spontaneous reaction between copper(II) ions and zinc metal in a galvanic cell:

\[ \text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq) \]

When standard half-cells are used, 1.1 volts may be generated by the cell.

If, however, an external DC power source is placed in the external circuit and connected so that the applied voltage is opposite to that generated by the galvanic cell, the reverse reaction proceeds:

\[ \text{Cu}(s) + \text{Zn}^{2+}(aq) \rightarrow \text{Cu}^{2+}(aq) + \text{Zn}(s) \]

When standard half-cells are used, more than 1.1 volts is needed to force this non-spontaneous reaction to occur.

Note (i): Although a knowledge of \( E^* \) values for cell half-reactions may enable a prediction to be made of the overall minimum voltage required for an electrolytic reaction to occur, the actual observed voltage may vary by as much as 1 volt, owing to a phenomenon known as ‘overpotential’. 

Note (ii): A full analysis of this situation would also involve the possibility that water molecules from the solution could also be ‘made’ to react. This is examined further later in this chapter.

In both galvanic and electrolytic cells, oxidation always occurs at the anode and reduction at the cathode.

In an electrolytic cell, the anode is positive and the cathode is negative.

Table 4.1 summarises the major similarities and differences between galvanic and electrolytic cells.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Galvanic cell</th>
<th>Electrolytic cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>type of redox reaction</td>
<td>spontaneous</td>
<td>non-spontaneous</td>
</tr>
<tr>
<td>energy produced or required</td>
<td>produced</td>
<td>required</td>
</tr>
<tr>
<td>where oxidation occurs</td>
<td>anode</td>
<td>anode</td>
</tr>
<tr>
<td>where reduction occurs</td>
<td>cathode</td>
<td>cathode</td>
</tr>
<tr>
<td>anode polarity</td>
<td>negative</td>
<td>positive</td>
</tr>
<tr>
<td>cathode polarity</td>
<td>positive</td>
<td>negative</td>
</tr>
<tr>
<td>how cell polarity is determined</td>
<td>depends on reactions occurring within cell</td>
<td>external power source</td>
</tr>
</tbody>
</table>
Comparison of zinc–copper half-cells in electrochemical and electrolytic reactions (a) Daniell cell showing fully labelled components, half-equations and overall equation (b) Electrolytic cell showing fully labelled components, half-equations and overall equation

A one-celled electrolytic cell. In an electrolytic cell, the two electrodes are usually immersed in a common electrolyte. In this example, the same reactions would occur if the electrolysis was carried out with copper and zinc electrodes immersed in a zinc sulfate solution.
Electrolysis of molten ionic compounds

The simplest cases of electrolysis involve the electrolysis of molten ionic substances that are pure, using inert electrodes. As an example, let us consider the electrolysis of molten sodium chloride.

Solid sodium chloride does not conduct electricity. However, when an electric current is passed through molten sodium chloride, a chemical reaction may be clearly observed. A shiny bead of sodium is produced at the cathode and chlorine gas is evolved at the anode.

In solid sodium chloride, the oppositely charged sodium ions, Na\(^+\), and chloride ions, Cl\(^-\), are held tightly together. Heating the solid causes the ions in the crystal to separate so they are then free to move. The molten liquid is called a melt. In an electrolytic cell, the sodium ions are attracted to the negative cathode where they are reduced:

Na\(^+\)(l) + e\(^-\) → Na(l)

The chloride ions are attracted to the positive anode where they undergo oxidation:

2Cl\(^-\)(l) → Cl\(_2\)(g) + 2e\(^-\)

Since, in a redox reaction, the same number of electrons are consumed as are produced, the overall equation is:

2Na\(^+\)(l) + 2Cl\(^-\)(l) → 2Na(l) + Cl\(_2\)(g)

Revision questions

1. Draw and label the apparatus you could use in the laboratory for the electrolysis of molten potassium chloride.
2. Explain why the reactants in a galvanic cell must be kept separated whereas the reactants in an electrolytic cell are usually contained within a single compartment.
**Electrolysis of water**

When a current is applied via two electrodes in pure water, nothing happens. There is no current flow and no electrolysis. If, however, an electrolyte such as H₂SO₄ or KNO₃ is added in low concentration, the resulting solution conducts electricity and electrolysis occurs. The products of the electrolysis of water, in this case, are hydrogen and oxygen.

At the cathode, water is reduced to form hydrogen:

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

At the anode, water is oxidised to form oxygen:

\[ 2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \]

The region around the cathode becomes basic owing to an increase in OH⁻ ions, whereas the region around the anode becomes acidic, owing to an increase in H⁺ ions. The overall cell reaction may be obtained by adding the half-equations:

\[ 6H_2O(l) \rightarrow 2H_2(g) + O_2(g) + 4H^+(aq) + 4OH^-(aq) \]

However, some of the ions produced re-form into reactants:

\[ 4H^+(aq) + 4OH^-(aq) \rightarrow 4H_2O(l) \]

and so do not need to be included in the final overall equation:

\[ 2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \]

**Electrolysis of aqueous solutions of ionic compounds**

When a molten salt is electrolysed, the products are predictable. However, as seen previously, when an aqueous solution of an ionic compound is electrolysed, water may react at one or both of the electrodes in preference to the ions from the salt. Hydrogen sometimes appears at the cathode, rather than a metal, and oxygen sometimes appears at the anode, rather than a metal cation or a halogen. For this reason, we need to be able to predict the products of electrolysis when there is more than one possible reaction around an electrode.

**Predicting reactions during electrolysis of aqueous solutions**

In aqueous solutions, there is a mixture of at least two oxidising agents and two reducing agents. If non-inert electrodes are used, then even more possibilities may exist. Which oxidising agent and which reducing agent react?

Although electrolytic products depend on a number of factors, the following procedure is useful.

1. List the species present, including all metals that are used as electrodes.
2. Write half-equations involving these species in descending order of \( E^* \).
3. Circle the species present in the electrolytic cell that could participate.
4. Select the oxidising agent with the highest \( E^* \) (the strongest oxidising agent). This will be reduced at the cathode, since it requires less energy for reduction than an oxidising agent with a lower \( E^* \).
5. Select the reducing agent with the lowest \( E^* \) (the strongest reducing agent). This will be oxidised at the anode, since it requires less energy for oxidation than a reducing agent with a higher \( E^* \).
6. Write the overall equation.
7. Determine the minimum voltage required to achieve the reaction by using the formula:

\[
\text{minimum voltage required} = E^{\circ}_{\text{oxidising agent}} - E^{\circ}_{\text{reducing agent}}
\]

Competing reactions are like wrestlers; the strongest challengers (strongest oxidising agent and strongest reducing agent) make it to the final round.

The electrolysis of dilute potassium iodide is shown above.

With potassium ions, iodide ions and water present in the cell, the possible half-cell reactions are:

- \( \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(l) \quad E^\circ = +1.23 \text{ V} \)
- \( \text{I}_2(s) + 2e^- \rightleftharpoons 2\text{I}^-(aq) \quad E^\circ = +0.54 \text{ V} \)
- \( 2\text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-(aq) \quad E^\circ = -0.83 \text{ V} \)
- \( \text{K}^+(aq) + e^- \rightleftharpoons \text{K(s)} \quad E^\circ = -2.93 \text{ V} \)

Reduction occurs at the cathode, so there are two possible reactions in this cell. The species that requires the least energy for reduction (the oxidising agent with the highest \( E^\circ \) value — the strongest oxidising agent) reacts at the cathode. So, water reacts in preference to potassium ions at the cathode:

\( 2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq) \quad E^\circ = -0.83 \text{ V} \)

Hydrogen gas is evolved at this electrode and the solution around the cathode becomes alkaline, owing to an increase in hydroxide ion concentration.

Oxidation occurs at the anode, so there are two possible reactions. The species that requires the least energy for oxidation (the reducing agent with the lowest \( E^\circ \) value) reacts at the anode. Thus, iodide ions react in preference to water molecules at the anode:

\( 2\text{I}^-(aq) \rightarrow \text{I}_2(s) + 2e^- \quad E^\circ = +0.54 \text{ V} \)

The solution around the anode appears yellow-brown, owing to the formation of iodine.

The overall electrolytic cell reaction would be:

\( 2\text{H}_2\text{O}(l) + 2\text{I}^-(aq) \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq) + \text{I}_2(s) \)
To achieve this reaction, a potential difference greater than the spontaneous reverse reaction would need to be applied. So more than $+0.54 - (-0.83) = 1.37$ volts should be delivered to this electrolytic cell.

The products formed from the electrolysis of some electrolytes are shown in Table 4.2.

**TABLE 4.2 Products of electrolysis**

(a) Using inert electrodes (platinum or graphite)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Product formed at cathode</th>
<th>Product formed at anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbBr$_2$(1) — a melt</td>
<td>Pb(s)</td>
<td>Br$_2$(g)</td>
</tr>
<tr>
<td>NaCl(1) — a melt</td>
<td>Na(s)</td>
<td>Cl$_2$(g)</td>
</tr>
<tr>
<td>CuCl$_2$(aq)</td>
<td>Cu(s)</td>
<td>Cl$_2$(g), O$_2^*$</td>
</tr>
<tr>
<td>NaCl(aq)</td>
<td>H$_2$(g)</td>
<td>Cl$_2$(g), O$_2^*$</td>
</tr>
<tr>
<td>KNO$_3$(aq)</td>
<td>H$_2$(g)</td>
<td>O$_2$(g)</td>
</tr>
<tr>
<td>CuSO$_4$(aq)</td>
<td>Cu(s)</td>
<td>O$_2$(g)</td>
</tr>
<tr>
<td>H$_2$SO$_4$(aq)</td>
<td>H$_2$(g)</td>
<td>O$_2$(g)</td>
</tr>
<tr>
<td>NaOH(aq)</td>
<td>H$_2$(g)</td>
<td>O$_2$(g)</td>
</tr>
</tbody>
</table>

*depending on concentration

(b) When the electrodes take part in the reaction

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Copper cathode</th>
<th>Copper anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO$_4$(aq)</td>
<td>Cu(s) deposited</td>
<td>Cu(s) dissolves to form Cu$^{2+}$ ions</td>
</tr>
</tbody>
</table>

The products formed during electrolysis depend on the concentration and nature of the electrolyte and the type of electrode used.

---

**Factors affecting electrolysis of aqueous solutions**

What happens during electrolysis depends on a number of factors, including:
- the concentration of the electrolyte
- the nature of the electrolyte
- the nature of the electrodes.

In any electrolysis reaction, alteration of any of these factors may change the nature of the products. The identity of products of an electrolysis reaction under fixed conditions is found by experiment. When the products are known, the reactions occurring at the electrodes may be written.

**The effect of concentration**

The electrochemical series (see Table 3.1 on page 80) is a very useful tool for predicting the products of an electrolysis reaction. It must be remembered, however, that it is based on standard conditions, in particular, where the concentrations of dissolved species are 1 M. If the concentrations of potential reactants are different from this, the observed results might be different from
those predicted. In the electrolysis of dilute sodium chloride, for example, reduction occurs at the cathode. The possible reactions are:

\[
2\text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-(aq) \quad E^* = -0.83 \text{ V} \\
\text{Na}^+(aq) + e^- \rightleftharpoons \text{Na}(l) \quad E^* = -2.71 \text{ V}
\]

As predicted from a table of standard redox potentials, water, rather than sodium ions, is reduced at the cathode. At the anode, chloride ions or water molecules may be oxidised:

\[
\text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^-(aq) \quad E^* = +1.36 \text{ V} \\
\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(l) \quad E^* = +1.23 \text{ V}
\]

As predicted from a table of standard redox potentials, oxygen gas is evolved in preference to chlorine gas at the anode.

The overall equation is:

\[
2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)
\]
(see electrolysis of water on page 113).

However, at higher concentrations (>6 M) of chloride ions, the discharge of chlorine becomes more favourable. The reduction of water, rather than sodium ions, still occurs at the cathode at higher concentrations of sodium ions. The electrolysis of dilute sodium chloride, therefore, produces hydrogen gas at the cathode and oxygen gas at the anode, but electrolysis of 6 M sodium chloride produces hydrogen gas at the cathode and chlorine gas at the anode.

This can be understood when the \( E^* \) values for the following reactions are examined:

\[
\text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^-(aq) \quad E^* = 1.36 \text{ V} \\
\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(l) \quad E^* = 1.23 \text{ V}
\]

These values change when conditions are non-standard. In fact, they change enough to swap the order around, thus making the oxidation of chloride ions to chlorine gas the preferred reaction at the anode. Such a reversal at the cathode does not occur because the difference between \( \text{H}_2\text{O} \) and \( \text{Na}^+ \) ions is too large.

Thus, when concentrated (>6 M) sodium chloride is electrolysed, the overall reaction becomes:

\[
2\text{H}_2\text{O}(l) + 2\text{Cl}^-(aq) \rightarrow \text{H}_2(g) + \text{Cl}_2(g) + 2\text{OH}^-(aq)
\]

**The nature of the electrolyte**

If concentrated copper(II) chloride solution, instead of concentrated sodium chloride solution, is electrolysed, the results are different.

At the anode, chlorine gas is evolved in both cells, since the solution is concentrated and the only species present initially are chloride ions and water molecules.

At the cathode, hydrogen gas is evolved in the sodium chloride cell, as discussed earlier. In the copper chloride cell, two reactions are possible at the cathode:

\[
\text{Cu}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cu}(s) \quad E^* = +0.34 \text{ V} \\
2\text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-(aq) \quad E^* = -0.83 \text{ V (−0.41 V at pH = 7)}
\]

As may be predicted from a consideration of the standard electrode potentials, copper is deposited in preference to the evolution of hydrogen gas.

So, the products in an electrolytic reaction depend on the nature of the electrolyte.
**The nature of the electrodes**

If the anode is made of a metal such as silver, copper or iron, electrons may be removed preferentially from the metal atoms in the electrode rather than from the ionic species in solution or the water molecules themselves.

There is no corresponding effect at the cathode because metals have no tendency to gain electrons.

The electrolysis of copper(II) chloride solution using inert electrodes, for example, results in the production of oxygen gas or chlorine gas (depending on the concentration of the solution; see table 4.2 on page 115) at the anode. However, if copper electrodes are used, copper(II) ions are produced at the anode, since the electrode itself acts as a stronger reducing agent than either water molecules or chloride ions:

\[
\text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^- (aq) \quad E^\circ = +1.36 \\
\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(l) \quad E^\circ = +1.23 \text{ V (at pH = 7)} \\
\text{Cu}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cu}(s) \quad E^\circ = +0.34 \text{ V}
\]

The copper anode dissolves to form Cu\(^{2+}\) ions.

In many electrolysis reactions, inert electrodes are used. Inert electrodes conduct a current but do not tend to go into solution as ions. Platinum metal and graphite are commonly used as inert electrodes.

**Revision questions**

3. Magnesium may be obtained commercially from sea water. During the last stage of this process, molten magnesium chloride undergoes electrolysis in a cell that contains an iron cathode and a graphite anode.

   (a) Why may iron be used to form the cathode but not the anode?
   (b) Draw a fully labelled diagram of an electrolytic cell that could be used to produce magnesium. Include equations.
4. A solution containing lead, magnesium and copper ions is electrolysed for a long time.
   (a) What will be the first product formed at the cathode?
   (b) If the electrolysis is continued until all the ions responsible for the product in (a) are used up, what will be the next product observed at the cathode?
   (c) If the electrolysis is continued further until the product from (b) is observed to stop forming, what will be the third product formed at the cathode?

5. Predict the products formed from the electrolysis, using inert electrodes, of:
   (a) molten lead (II) chloride
   (b) a 1 M solution of lead (II) chloride

**Commercial applications of electrolysis**

The principles discussed so far for electrolytic cells can be applied in industry to many important and familiar processes. Electrolysis provides the only practical way to prepare many metals, such as aluminium and metals from groups 1 and 2. Reactive gases such as fluorine and chlorine are also prepared by this method, along with the industrially important chemical sodium hydroxide. The process of electroplating objects is no doubt familiar where a thin coating of metal is applied to a more common ‘base’ metal, and today’s need for ultrapure copper in the electronics industry is provided by electrorefining.

**Producing aluminium**

Although aluminium is the most abundant metallic element in the Earth’s crust, its extraction before 1886 proved very difficult. The most common process involved its extraction from the ore and conversion into AlCl$_3$. This was then chemically reduced using either sodium or potassium, metals that were also difficult to produce. Compared with today’s methods, this process was on a small scale and very expensive. In fact, aluminium metal was considered more expensive than gold!

The breakthrough came in 1886 with the development of what we now call the Hall–Héroult cell.

**Hall–Héroult cell**

Working independently of each other, Paul Héroult in France and Charles Hall in the USA almost simultaneously filed patent applications for the industrial electrolytic production of aluminium. Today, the Hall–Héroult method of aluminium production is used in primary aluminium smelters throughout the world. It has resulted in an enormous growth in aluminium production from 13 tonnes per year in 1885 to more than 25 million tonnes per year today.

The industrial production of aluminium occurs in a Hall–Héroult cell (shown on the next page) and involves electrolysis of alumina that is dissolved in molten cryolite. The electrolysis takes place in a steel vessel called a cell. The cell is lined with carbon and contains the molten cryolite and dissolved alumina mixture maintained at a temperature of about 980 °C. Carbon blocks that are suspended above the cell and are partially immersed in the electrolyte act as anodes, while the carbon lining of the cell acts as the cathode.

Today, aluminium is produced by electrolysis in a Hall–Héroult cell.
Aluminium cannot be reduced by electrolysis of an aqueous aluminium salt because water would be preferentially reduced.

Cryolite acts as a solvent and an electrolyte. Its use allows the cell to operate at a lower temperature than using alumina alone.

The carbon anodes are consumed in the process.

Aluminium settles at the bottom of the cell and is siphoned out.

Aluminium cannot be reduced by electrolysis of an aqueous solution of a soluble aluminium salt because water, a stronger oxidising agent than aluminium ions, is preferentially reduced:

\[
2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^- (\text{aq}) \quad E^* = -0.83 \text{ V}
\]

\[
\text{Al}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Al}(s) \quad E^* = -1.67 \text{ V}
\]

Cryolite, \( \text{Na}_3\text{AlF}_6 \), acts as a solvent and an electrolyte. Its role is due to its unique combination of properties; it has a melting point less than half that of alumina (960 °C compared with alumina's 2020 °C), a low vapour pressure and a density lower than molten aluminium's (2.05 g cm\(^{-3}\) compared with aluminium's 2.30 g cm\(^{-3}\)). Cryolite can dissolve sufficient alumina to allow deposition of aluminium at about 980 °C. Less energy is used, saving the industry fuel costs.

The carbon anode and cathode are both made from petroleum coke with pitch as a binder. The anode takes part in the chemical reactions in the cell.

Alumina is fed into the electrolyte at regular intervals where it dissolves, forming aluminium ions, \( \text{Al}^{3+} \), and oxide ions, \( \text{O}^{2-} \). The direct current applied across each cell moves the ions in opposite directions.

At the anode, the oxide ions are oxidised to form oxygen gas. The oxygen then immediately reacts with the carbon anode to form carbon dioxide.

Anode reactions:

\[
2\text{O}^2-(l) \rightarrow \text{O}_2(g) + 4e^-
\]

\[
\text{O}_2(g) + \text{C}(s) \rightarrow \text{CO}_2(g)
\]

As the carbon anodes are gradually consumed during the process, they are lowered to maintain the optimum distance between the anode and cathode surfaces, until they are burned away and replaced. The anodes are generally replaced every 3 weeks so that the process is continuous.

The positively charged aluminium ions that are dissolved in the cryolite are drawn to the negatively charged cathode where they form aluminium.

Cathode reaction:

\[
\text{Al}^{3+}(l) + 3e^- \rightarrow \text{Al}(l)
\]

The density difference between cryolite and newly formed molten aluminium allows the aluminium to settle at the bottom of the cell where it is regularly siphoned out. After siphoning, the molten aluminium may be cast.
The overall reaction for the electrolytic production of aluminium by electrolysis can be represented as:

$$2\text{Al}_2\text{O}_3(\text{l}) + 3\text{C}(\text{s}) \rightarrow 4\text{Al}(\text{l}) + 3\text{CO}_2(\text{g})$$

The gases produced in this process are mainly carbon dioxide. Other gases include fluorides that are initially confined by gas hoods, then continuously removed and treated.

The amount of alumina added to a cell must be strictly controlled. If too little alumina is added, maximum yields and productivity rates of aluminium production become economically unfavourable. If too much alumina is added, it does not dissolve. Instead it falls to the bottom of the cell (since it is denser than molten aluminium) where it settles below the aluminium and interferes with the flow of current.

Hall–Héroult cells operate continuously at low voltage of about 4–5 V but require a high current of 50 000–280 000 A. The excess voltage and the heat of combustion of carbon are used to keep the electrolyte in a liquid state.

**Industrial electrolysis of brine**

Chlorine gas, hydrogen gas and sodium hydroxide are three important industrial chemicals. They may be produced simultaneously by electrolysis of a concentrated aqueous sodium chloride solution (brine). Recently, a new type of electrolytic cell, the **membrane cell**, was developed for this reaction.

Although chloride ions are weaker reducing agents than water molecules, chlorine may be produced electrolytically from aqueous solutions of sodium chloride by altering the operating conditions of electrolytic cells to favour the reduction of chloride ions rather than water molecules.

**Membrane cells**

Early cells for the electrolysis of brine used either mercury or asbestos in their design. Membrane cells were developed in response to the potential health hazards involved with such cells. Industrial membrane cells can be very large.

A membrane cell is characterised by its plastic, semipermeable membrane that separates the anode half-cell from the cathode half-cell of the electrolytic cell. This semipermeable membrane allows sodium ions and electricity to pass from one electrode half-cell to another but does not allow chloride ions to pass through.
ions or water to pass through. As a result, sodium ions and hydroxide ions are trapped in the cathode compartment, thus producing pure sodium hydroxide along with hydrogen gas, which is evolved at the cathode itself. Chlorine gas is produced at the anode. The relevant equations are as follows.

**Cathode:**

\[ 2\text{Na}^+(aq) + 2\text{H}_2\text{O}(l) + 2e^- \rightarrow 2\text{NaOH}(aq) + \text{H}_2(g) \]

**Anode:**

\[ 2\text{Cl}^-(aq) \rightarrow \text{Cl}_2(g) + 2e^- \]

As with all electrolytic cells, the products are prevented from coming into contact with each other (this would result in a spontaneous redox reaction, which would re-form the reactants!). The overall reaction for the production of chlorine via the membrane cell process is:

\[ 2\text{NaCl}(aq) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{NaOH}(aq) + \text{H}_2(g) + \text{Cl}_2(g) \]

**Revision questions**

6. The addition of cryolite, \( \text{Na}_3\text{AlF}_6 \), in the Hall–Héroult process introduces \( \text{Na}^+(l) \) and \( \text{F}^-(l) \) into the mixture. Why is there no issue with contamination?

7. Cryolite is added to lower the melting temperature of alumina and, therefore, use less energy for the process of obtaining aluminium. Why does alumina, \( \text{Al}_2\text{O}_3 \), have such a high melting point (2020 °C)?

**Electroplating**

Electroplating is the coating of an object with a thin film of metal deposited by an electrolytic solution during electrolysis. Electroplating is often used to produce an attractive and durable finish on articles such as knives and forks (silver plate). It is also used to protect corrosion-prone metals. Relatively unreactive cadmium metal, for example, is often plated onto steel parts to inhibit rusting. Electroplating is a very valuable industrial process but its use requires costly and consistently effective treatment of the wastes it produces.

Inexpensive silver-plated jewellery may be produced through electroplating. ‘Gold’ rings, which cause fingers to turn green, are actually copper rings that have been electroplated with gold.

In the electroplating process, the article to be plated is used as the cathode and the metal being plated onto the article is used as the anode. The electrolytic solution or ‘bath’ contains a salt of the metal being plated. A low-voltage
electric current causes metal ions from the bath to gain electrons at the cathode and to deposit as a metal coating on the cathode (the object). It also causes metal atoms in the anode to lose electrons and go into the bath as ions. As the plating proceeds, the anode gradually disappears and maintains the metal ion's concentration in the bath.

Electroplating operations involve the use of many toxic solutions. Objects to be plated are thoroughly cleaned of all grease and dirt using concentrated acidic or basic solutions. The cleaning solutions eventually become ineffective, owing to contamination, and must be disposed of.

A number of factors contribute to the quality of the metal coating formed in electroplating:

- In the plating solution, the concentration of the cations to be reduced is carefully controlled. Unwanted side reactions must be avoided.
- The type and concentration of electrolyte needs careful consideration.
- The solution must contain compounds to control the acidity and increase the conductivity.
- Some compounds make the metal coating brighter or smoother.
- In many electroplating cells, the anode must be shaped like the object at the cathode to achieve an even metal coating.

**Silver-plating**

In silver-plating, objects such as cutlery are made the cathode. The plating solution contains silver ions, $\text{Ag}^+(\text{aq})$. The anode is pure silver. When current flows, silver is deposited on the metal object:

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

At the same time, silver atoms at the anode form silver ions:

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

You will notice that the above reactions are possible due to their positions on the electrochemical series relative to water. At the cathode, silver ions are a stronger oxidising agent than water and so they are preferentially reduced. At the anode, silver metal is a stronger reducing agent than water. The silver metal, therefore, reacts in preference to water and is oxidised to silver ions.

The plating is only a few hundredths of a centimetre thick. If the experimental conditions are right, the metal coating adheres strongly and may be polished. However, if conditions are not satisfactory, the metal becomes powder-like and drops off.

A silver-plated trophy for the winner

Silver-plating mechanism for cutlery
Calculations in electrolysis — Faraday’s laws

Michael Faraday

Michael Faraday (1791–1867) was a bookbinder by trade who became an assistant to the English chemist Sir Humphrey Davy. Although the job was menial, he advanced quickly, gaining a reputation for dedication and thoroughness.

Faraday first learned about the phenomenon of electricity from an article in an encyclopedia that was brought to his employer for rebinding. His interest in science was kindled and he became an avid reader of scientific papers, in addition to attending lectures on science. Furthermore, he wrote complete notes on every book he read and every lecture he attended.

Faraday began working as an assistant at the Royal Institution and, after 10 years of hard work, began his own research in analytical chemistry. He discovered benzene in 1825 and was the first person to produce compounds of carbon and chlorine in the laboratory. However, he is most famous for his work on electricity and, in 1833, he published the results of his studies of electrolysis. Faraday had made careful measurements of the amount of electricity involved during electrolysis and related it to the amount of substances produced. His work established two ‘laws’ of electrochemistry. The amount of charge carried by 1 mole of electrons is called a faraday in honour of Michael Faraday’s contribution to science.

Faraday’s first law of electrolysis

Faraday’s first law of electrolysis may be stated as follows:

The amount of any substance deposited, evolved or dissolved at an electrode during electrolysis is directly proportional to the quantity of electric charge passed through the cell.

The quantity of electric charge transferred by an electric current depends on the magnitude of the current used and the time for which it flows. The electric charge can be calculated using the formula:

\[ Q = It \]

where \( Q \) is the electrical charge in coulombs (C)

\( I \) is the current in amperes (A)

\( t \) is the time in seconds (s).

In an experimental circuit, there is no meter that measures the charge in coulombs. However, an ammeter could be used to measure the rate at which charge flows in a circuit. A current of 1 ampere (1 A) indicates that 1 coulomb (6.24 × 10^{18} electrons) of charge flows every second. (Note: Current is symbolised by the letter \( I \).)

If, for example, a current of 3.00 amperes flows for 10.0 minutes, the quantity of electricity is (3.00 × 10.0 × 60) = 1.80 × 10^{3} coulombs. The charge flowing through an electrolytic cell can be increased by either increasing the magnitude of the current or by increasing the time.
In an experiment to investigate the relationship between the quantity of electricity and the mass of electrolytic products, copper(II) sulfate was electrolysed using copper electrodes. The copper cathode was weighed before the electrolysis. Then, after 10.0 minutes of electrolysis with a current of 3.00 amperes, the experiment was stopped and the cathode reweighed. The mass of copper deposited was calculated, the cathode was replaced, and the experiment continued for another 10.0 minutes. The mass of copper deposited in 20.0 minutes was then found. This procedure was repeated several times, and the results obtained are shown in table 4.3.

A graph of these results yields a straight line passing through the origin, showing that the mass of the product is directly proportional to the quantity of electricity. The mass of copper deposited on the cathode during electrolysis is directly proportional to the quantity of electricity used.

### Table 4.3

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>Time (s)</th>
<th>Quantity of electricity (C)</th>
<th>Mass of copper (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.00</td>
<td>600</td>
<td>1800</td>
<td>0.59</td>
</tr>
<tr>
<td>3.00</td>
<td>1200</td>
<td>3600</td>
<td>1.19</td>
</tr>
<tr>
<td>3.00</td>
<td>1800</td>
<td>5400</td>
<td>1.78</td>
</tr>
<tr>
<td>3.00</td>
<td>2400</td>
<td>7200</td>
<td>2.38</td>
</tr>
</tbody>
</table>

The charge on one electron is $1.602 \times 10^{-19}$ C. One mole of electrons, therefore, has a charge of $(6.023 \times 10^{23} \times 1.602 \times 10^{-19}) = 9.649 \times 10^4$ C. This quantity of charge carried by a mole of electrons is referred to as the faraday (F), or Faraday constant, and is usually given the value of 96,500 C mol$^{-1}$.

**Faraday’s second law of electrolysis**

Faraday’s second law of electrolysis may be stated as follows:

In order to produce 1 mole of a substance by electrolysis, 1, 2, 3 or another whole number of moles of electrons (faradays) must be consumed, according to the relevant half-cell equation.

In the half-cell equation:

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

1 mole of silver ions 1 mole of electrons 1 mole of silver atoms

1 mole of electrons is needed to discharge 1 mole of Ag$^+(\text{aq})$ ions. This liberates 1 mole of silver atoms. Thus, 1 faraday, or 96,500 coulombs, is needed to discharge 1 mole of silver atoms.

The number of faradays (moles of electrons) needed to liberate 1 mole of an element during electrolysis is found from the equation for the electrode reaction. Some examples are given below.

**Sodium**: $\text{Na}^+ + e^- \rightarrow \text{Na}$

1 faraday must be passed to liberate 1 mole of sodium atoms (23.0 g).

**Copper**: $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$

2 faradays must be passed to liberate 1 mole of copper atoms (63.5 g).

**Magnesium**: $\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$

2 faradays must be passed to liberate 1 mole of magnesium atoms (24.3 g).
Aluminium: \( \text{Al}^{3+} + 3e^- \rightarrow \text{Al} \) 3 faradays must be passed to liberate 1 mole of aluminium atoms (27.0 g).

Chlorine: \( 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \) 2 faradays must be passed to liberate 1 mole of chlorine molecules (71.0 g).

So, the number of moles of electrons, \( n(\text{electrons}) \), corresponding to a given charge may be determined as follows:

\[
\text{n(electrons)} = \frac{Q}{F}
\]

**Applying Faraday’s laws of electrolysis**

Most calculations in electrolysis involve finding the mass of a metal deposited on an electrode, the mass or volume of a gas produced, or the charge of an ion in the electrolytic reaction. Such problems may be solved by using the following formulas:

\[
Q = It
\]

\[
\text{n(electrons)} = \frac{Q}{F}
\]

where \( Q \) is the electrical charge (C), \( I \) is the current (A), \( t \) is the time (s) and \( F = 96500 \text{ C mol}^{-1} \).

These relationships summarise Faraday’s two laws of electrolysis.

**Sample problem 4.1**

A solution of copper(II) sulfate is electrolysed for 30.0 minutes using a current of 0.500 A. Calculate:

(a) the mass of copper deposited on the cathode
(b) the volume (at SLC) of oxygen gas evolved at the anode.

**Solution:** The amount of electricity (\( Q \)) used = \( I(A) \times t(s) \)

\[
= 0.500 \times 30.0 \times 60
\]

\[
= 900 \text{ coulombs}
\]

(a) At the cathode:

\[
\text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu(s)}
\]

The number of moles of electrons, \( n(\text{electrons}) = \frac{Q}{F} \)

\[
= \frac{900 \text{ C}}{96500 \text{ C mol}^{-1}}
\]

\[
= 0.00932 \text{ mol}
\]

But, from the equation, the number of moles of copper formed equals half the number of electrons used, thus:

\[
\text{n(Cu)} = \frac{1}{2} \times 0.00932 \text{ mol}
\]

\[
= 0.00466 \text{ mol}
\]

Therefore, mass of copper = \( 0.00466 \text{ mol} \times 63.5 \text{ g mol}^{-1} \)

\[
= 0.296 \text{ g}
\]

Hence, the mass of copper deposited is 0.296 g.
(b) At the anode:
\[ 2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \]

\[ n(\text{electrons}) = \frac{900 \text{ C}}{96500 \text{ C mol}^{-1}} = 0.0093 \text{ mol} \]

But, from the equation:

\[ n(\text{O}_2) = \frac{1}{4} n(\text{electrons}) \]

\[ = \frac{1}{4} \times 0.0093 \text{ mol} = 0.0012 \text{ mol} \]

Therefore, the volume of oxygen at SLC = \[ n \times V_M \]

\[ = 0.0012 \text{ mol} \times 24.8 \text{ L mol}^{-1} = 0.0578 \text{ L} \]

Hence, 57.8 mL of oxygen is produced at SLC.

**Revision questions**

8. Calculate the mass of iron deposited at the cathode when a solution of iron(II) nitrate undergoes electrolysis for 1 hour 20 minutes using a current of 0.75 A.

9. Calculate the volume (at SLC) of oxygen gas evolved at the anode when a dilute solution of nickel(II) sulfate undergoes electrolysis for 3 hours 25 minutes using a current of 0.40 A.

10. What mass of each of the following substances can be produced in 2.00 hours with a current of 12.0 A?
   (a) Co from aqueous Co\(^{3+}\)
   (b) I\(_2\) from aqueous I\(^-\)
   (c) Cr from molten CrO\(_3\)

11. How long will it take to produce each of the following by electrolysis with a current of 80.0 A?
   (a) 1.00 kg of Ni(s) from Ni\(^{2+}\)
   (b) 2.50 g of Al(s) from Al\(^{3+}\) in a melt
   (c) 5.25 mol of Ag(s) from Ag\(^+\)

**Sample problem 4.2**

When molten calcium chloride is electrolysed by a current of 0.200 A flowing for 965 seconds, 0.0401 g of calcium is formed. What is the charge on a calcium ion?

**Solution:**

The amount of electricity \((Q)\) used is:

\[ Q = It \]

\[ = 0.200 \text{ C s}^{-1} \times 965 \text{ s} = 193 \text{ C} \]

The number of moles of electrons used is:

\[ n(\text{electrons}) = \frac{Q}{F} \]

\[ = \frac{193 \text{ C}}{96500 \text{ C mol}^{-1}} = 0.00200 \text{ mol} \]
The number of moles of calcium formed is:

\[ n(Ca) = \frac{0.0401}{40.1 \text{ g mol}^{-1}} = 0.001 \text{ mol} \]

Therefore, 0.002 00 mol of electrons are needed to liberate 0.001 00 mol of calcium. The ratio is:

\[
2 \text{ electrons} : 1 \text{ calcium ion} \\
Ca^{2+} + 2e^- \rightarrow \text{Ca}
\]

So, the charge on a calcium ion is 2+.

**Revision questions**

12. When molten manganese nitrate was electrolysed by a current of 5.00 A for 884 seconds, the mass of the cathode increased from 2.428 g to 3.267 g. Calculate the charge on the manganese ion in the nitrate salt.

13. When a current of 0.0600 A flowed through an electrolytic cell for 1 hour and 6.00 minutes, the mass of the cathode increased by 0.254 g due to the deposition of a metal with a relative atomic mass of 207. Calculate the charge on a cation of this metal.

**Faraday’s laws in industry**

Calculations based on Faraday’s laws are critical to industrial electrolytic processes. Due to their large scale, small variations and inefficiencies may result in the loss of many thousands of dollars. In order to determine the efficiency of a particular process, knowledge of the theoretical maximum amount is required.

**Sample problem 4.3**

A typical Hall–Héroult cell in an aluminium plant operates at an average current of \(1.70 \times 10^4\) A. Calculate the theoretical mass of aluminium produced in a Hall–Héroult cell over 24 hours.

**Solution:**

The amount of electricity can be calculated according to:

\[ \text{charge} (Q) = \text{current} (I) \times \text{time} (t) \text{ in seconds} \]

\[ = 1.70 \times 10^4 \times 60 \times 60 \times 24 \]

\[ = 1.47 \times 10^9 \text{ coulombs} \]

At the cathode: \(Al^{3+}(l) + 3e^- \rightarrow Al(l)\)

So, \(n(\text{electrons}) = \frac{Q}{F}\)

\[ = \frac{1.47 \times 10^9}{96500} \]

\[ = 1.52 \times 10^4 \text{ mol} \]

From the equation, the amount of aluminium formed corresponds to one-third of the number of electrons generated, so:

\[ n(Al) = \frac{1}{3} \times 1.52 \times 10^4 \]

\[ = 5.07 \times 10^3 \text{ moles of Al} \]
The theoretical mass of aluminium produced is therefore:

\[
\text{mass(Al)} = n(\text{Al}) \times A_r(\text{Al}) \\
= 5.07 \times 10^3 \times 27.0 \\
= 1.37 \times 10^5 \text{ g} \\
= 1.37 \times 10^2 \text{ kg}
\]

Revision question

14. For a Hall–Héroult cell in an aluminium plant operating at an average of 180,000 A, calculate:
   (a) the theoretical mass of aluminium produced in a Hall–Héroult cell per hour
   (b) how long it would take for the cell to produce 10.0 kilograms of aluminium
   (c) the volume of carbon dioxide, measured at SLC, produced per day by the cell.

Secondary cells — rechargeable batteries

Secondary cells, often referred to simply as rechargeable batteries, are devices that can be recharged after they become ‘flat’. They are essentially galvanic cells using spontaneous redox reactions to produce electricity during discharge, but they become electrolytic cells converting electrical energy back into chemical energy when they are recharged. To enable this to happen, they are designed so that the discharge products remain in contact with the electrodes at which they are produced. The process of recharging simply involves connecting the negative terminal of the charger to the negative terminal of the battery or cell, and the positive to the positive. This forces the electrons to travel in the reverse direction and, because the discharge products are still in contact with the electrodes, the original reactions are reversed. The cell or battery is, therefore, recharged.

The lead–acid accumulator is a common example of a secondary cell that has been widely used for many years. Other smaller more portable designs are now familiar to us. Although initially more expensive than the primary cells they are designed to replace, their ability to be recharged many hundreds of times makes them a cheaper alternative in the long run.

Lead–acid accumulator

Developed in the late nineteenth century, the lead–acid accumulator, an example of a secondary cell, has remained the most common and durable of battery technologies. Lead–acid accumulators are secondary cells. They have a relatively long lifetime and high current, and they are cheap to produce. Largely used in transport applications, they rely on a direct current generator or alternator in the vehicle to apply enough voltage to reverse the spontaneous electrochemical reaction that helps to ‘drive’ the car.

A 12-volt lead–acid storage battery consists of six 2-volt cells connected in series. The cells do not need to be in separate compartments, although this improves performance.

Each cell consists of two lead electrodes or grids. The grid structure provides a larger surface area for electrode reactions. The grid that forms the anode
(negative terminal) of the cell is packed with spongy lead. The other grid, the cathode (positive terminal), is packed with lead(IV) oxide, PbO₂. The electrodes are both immersed in approximately 4 M sulfuric acid and are separated by a porous plate.

![Chemical energy is converted to electrical energy when the battery discharges.](image)

The discharging process in a lead–acid accumulator

When a lead–acid accumulator discharges, it produces electric power to start the car. Discharge results from a spontaneous redox reaction.

The half-equations at each electrode may be written as follows.

Anode (oxidation):

\[ \text{Pb(s)} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4(s) + 2e^- \]

Cathode (reduction):

\[ \text{PbO}_2(s) + 4\text{H}^+(aq) + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O(l)} \]

At the anode (negative electrode), lead is oxidised to Pb²⁺ ions. These react immediately with the sulfuric acid solution to produce insoluble lead(II) sulfate, which deposits on the grid.

At the cathode (positive electrode), lead(IV) oxide is reduced to Pb²⁺ ions, which again react with the sulfuric acid to form a lead(II) sulfate deposit on the grid. The overall equation for the discharging reaction is:

\[ \text{PbO}_2(s) + 4\text{H}^+(aq) + \text{Pb(s)} + 2\text{SO}_4^{2-} \rightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O(l)} \]

*Note:* The pH of the cell increases during the discharge cycle.

The recharging process in a lead–acid accumulator

Since the products of the discharge process remain as a deposit on the electrodes, the reactions at these electrodes may be reversed by passing a current through the cell in the opposite direction. The battery is then said to be recharging. When the battery is recharged, the electrode reactions are reversed by connecting the terminals to another electrical source of higher voltage and reversing the direction of the electric current through the circuit. Recharging occurs while the car is in motion.
During recharging, the flow of $e^-$ is reversed and the electrode forming the negatively charged anode in the discharging process becomes the negatively charged cathode, where reduction occurs.

Cathode (reduction):

$$\text{PbSO}_4(s) + 2e^- \rightarrow \text{Pb}(s) + \text{SO}_4^{2-}(aq)$$

The electrode previously forming the positively charged cathode in the discharging process now becomes the positively charged anode, where oxidation occurs, in the recharging process.

Anode (oxidation):

$$\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{PbO}_2(s) + \text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2e^-$$

The overall reaction for the recharging process is therefore the reverse of the discharging process.

$$2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{PbO}_2(s) + 4\text{H}^+(aq) + \text{Pb}(s) + 2\text{SO}_4^{2-}(aq)$$

*Note:* The pH of the cell decreases during the recharge cycle.

Since this reaction is not spontaneous, a direct current must be applied in order for it to proceed. This is achieved by the alternator (a motor-driven electrical source of higher voltage than the battery), which has a potential difference of 14 V. The recharging process converts electrical energy into chemical energy and is an example of an electrolytic reaction.

Although, in theory, a lead storage battery can be recharged indefinitely, in practice it may last for only about four years. This is because small amounts of lead(II) sulfate continually fall from the electrodes and drop to the bottom...
of the cell. Eventually, the electrodes lose so much lead(II) sulfate that the recharging process is ineffective.

The disposal of lead–acid batteries poses many environmental problems. Lead is poisonous when introduced into most ecosystems, and the impact of acid rain is distinct and measurable. Once disposed of in landfill or illegally dumped, lead–acid batteries may corrode and release lead and lead-contaminated sulfuric acid into the environment. This can pollute drinking water sources such as lakes, rivers, streams and ground water. Responsible lead–acid battery reclaiming and recycling projects now allow for safe disposal of used batteries.

**Nickel metal hydride rechargeable cell**

Although the nickel cadmium (NiCd) cell was the first rechargeable cell to find widespread use in many common household devices, it has largely been replaced today by the nickel metal hydride (NiMH) cell. This shares a number of features with the NiCd cell but is environmentally safer due to the absence of cadmium. A problem with NiCd cells was the so-called memory effect. If the cell was only partially discharged before recharging occurred, it would not receive a full charge. NiMH cells show much less of this effect. They also have nearly 50% more charge per gram, can recharge faster and can run longer on each charge.

The reactions involved during discharge to produce an electric current are as follows.

Oxidation takes place at the negative electrode (anode):

\[
\text{MH} (\text{s}) + \text{OH}^- (\text{aq}) \rightarrow \text{M} (\text{s}) + \text{H}_2\text{O} (\text{l}) + e^- \quad \text{note the M here refers to a metal}
\]

Reduction takes place at the positive electrode (cathode).

\[
\text{NiO(OH)} (\text{s}) + \text{H}_2\text{O} (\text{l}) + e^- \rightarrow \text{Ni(OH)}_2 (\text{s}) + \text{OH}^- (\text{aq})
\]

Overall equation:

\[
\text{NiO(OH)}(\text{s}) + \text{MH}(\text{s}) \rightleftharpoons \text{Ni(OH)}_2(\text{s}) + \text{M} (\text{s})
\]

Nickel metal hydride batteries are similar to nickel–cadmium batteries except that a hydrogen-absorbing metal is used as the anode. These metals (M) can be alloys of lanthanum and rare earths. The electrolyte is potassium hydroxide and the voltage produced is 1.2 volts.

Nickel metal hydride batteries have many advantages but also some disadvantages. They suffer from self-discharge — a problem that is worse at higher temperatures — and require more complicated charging devices to prevent overcharging.

They are used in laptops, electric shavers, toothbrushes, cameras, camcorders, mobile phones and medical instruments, and are being developed for car batteries.

**Rechargeable lithium ion cell**

The lithium ion cell, which uses lithium compounds rather than lithium metal, is rapidly becoming the most popular choice of battery for portable devices. It consists of a porous graphite anode and a porous metal oxide cathode in an electrolyte of lithium salt held in an organic solvent. Lithium is interspersed between the layers of graphite. At the cathode, a commonly used material is cobalt(IV) oxide containing some lithium ions stored in the gaps of its lattice structure. As a result of this, cobalt is present in both the +4 and +3 oxidation states. When the cell is discharging, lithium atoms readily release electrons into the graphite...
anode because lithium is such a good reducing agent. The lithium ions produced travel internally to the cathode where they insert into the cobalt oxide lattice. At the same time, electrons arrive from the external circuit, and further reduction of cobalt from the $+4$ to $+3$ oxidation state takes place.

The structure of a lithium ion cell

The equations are as follows.

Cathode (reduction):
$$\text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \rightarrow \text{LiCoO}_2$$

Anode (oxidation):
$$\text{CLi}_x \rightarrow \text{C} + x\text{Li}^+ + xe^-$$

Overall equation:
$$\text{Li}_{1-x}\text{CoO}_2 + \text{CLi}_x \rightarrow \text{LiCoO}_2 + \text{C}$$

These cells are expensive to produce but now are extensively used in mobile phones, laptops, cameras, heart defibrillators, mobile radios, power tools and vehicles.

During the operation of a lithium ion cell, lithium ions move from the anode to the cathode.
Lithium ion cells have a good shelf life and a very high energy density; they supply a voltage of about 3.7 volts, which is more than double that of most other cells. However, their state of charge needs to be monitored carefully. If they are overdischarged, they cannot be recharged. On the other hand, if they are overcharged, serious safety concerns may arise. To prevent both of these extremes, they are nearly always produced with a protection circuit that prevents both of these situations from arising. This, however, adds to their cost.

Revision questions

15. What feature of a lead–acid accumulator allows it to be recharged?
16. Would the pH of the electrolyte in a lead–acid accumulator increase or decrease during recharge?
17. Why is a porous graphite electrode used in a lithium ion cell?
18. Examine the power cell in a mobile phone or other small electronic device. What type of cell is it? Make a list of the advantages of this type of cell for this application.
19. Write the overall equation for the recharging process in a nickel metal hydride cell.
20. In the nickel–cadmium cell, the cathode reaction is the same as in the nickel metal hydride cell during discharge. The anode reaction is:

\[ \text{Cd(s)} + 2\text{OH}^- (\text{aq}) \rightarrow \text{Cd(OH)}_2(s) + 2\text{e}^- \]

Write the overall equation for the discharge of this cell.

Factors affecting battery life

While there are specialist batteries designed to operate at extreme temperatures, the great majority of batteries used today are designed to operate over an optimum range of temperatures that encompass normal room temperature. If they are used outside this range, breakdowns in both the electrochemistry and their physical components may occur, rendering the battery inoperative and even dangerous.

Each battery type also has its own specific problems related to temperature and componentry. In a lead–acid accumulator, for example, overdischarge thickens the layers of lead sulfate that build up on the electrodes. Particles can break off and fall to the base of the cell, thereby lowering the amount remaining for recharge. In extreme cases, due to the closeness of the electrodes, internal
short circuits may also occur if the insulation is damaged and the electrodes touch. At low temperatures, especially if the sulfuric acid content is low (because of a low state of charge), the electrolyte may even freeze and cause damage to the battery on expansion. If temperatures are too high, due to over-charging or the operating environment, the plates (electrodes) may buckle, damaging the insulation between them and possibly leading to internal short circuits.

In a lithium ion battery, the situation is even more complex and potentially dangerous, with an internal protective circuit required for consumer safety. To avoid problems, lithium batteries must operate within a narrow window of both temperature and voltage, as shown by the green area in the diagram below.

At low temperatures, insertion of lithium ions into the lattice spaces at the anode and cathode can become difficult due to contraction reducing the physical size of these spaces. During the charging process, this may cause lithium metal to be deposited on the graphite electrode for the same reason, thus lowering the amount of electricity that can be generated by the cell following subsequent recharge cycles.

Operation of lithium ion cells at temperatures that are too high can cause ‘thermal runaway’. This includes a number of stages that involve exothermic reactions, with each stage becoming progressively more serious.

- As with most chemical reactions, an increase in temperature increases the rate of reactions that produce the electricity. However, due to the internal resistance of the cell, this can generate excessive heat and break down the SEI (solid electrolyte interface) layer. This layer is initially formed by an exothermic reaction between the electrolyte and the graphite electrode under carefully controlled conditions during manufacture. If it is subsequently broken down, this same reaction may recur, but this time in a much more uncontrolled manner, resulting in heat generation and further temperature rise.
- These higher temperatures can then break down organic materials in the electrolyte, producing flammable gases such as methane and ethane. Although these gases do not burn due to the absence of oxygen, they do cause a build-up of pressure within the cell and may need to be vented via special safety valves built into the cell.
- Further temperature increase results in the polymer separator between the anode and the cathode melting, causing short circuiting.
- Finally, once the temperature reaches about 200 °C, the metal oxide cathode begins to break down, releasing oxygen gas. Ignition quickly follows.
Summary

- Electrolysis is the process by which electricity passes through a molten ionic compound or through an electrolyte solution to produce new substances.
- The apparatus in which electrolysis occurs is called an electrolytic cell.
- Solutes that form solutions that can conduct electricity are called electrolytes.
- In electrolysis, positive ions gain electrons at the cathode (negative electrode) and negative ions lose electrons at the anode (positive electrode).
- Electrolytic cells differ from galvanic cells in a number of ways, as summarised in the following table.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Galvanic cell description</th>
<th>Electrolytic cell description</th>
</tr>
</thead>
<tbody>
<tr>
<td>type of reaction</td>
<td>spontaneous redox reaction</td>
<td>non-spontaneous redox reaction</td>
</tr>
<tr>
<td>energy</td>
<td>produce electricity</td>
<td>require energy</td>
</tr>
<tr>
<td>structure</td>
<td>two half-cells connected by a wire (external circuit) and a salt bridge (internal circuit)</td>
<td>one cell, connecting wires and an external power supply (e.g., battery, DC power supply)</td>
</tr>
<tr>
<td>anode</td>
<td>negatively charged, oxidation</td>
<td>positively charged, oxidation</td>
</tr>
<tr>
<td>cathode</td>
<td>positively charged, reduction</td>
<td>negatively charged, reduction</td>
</tr>
<tr>
<td>source of electrons</td>
<td>reducing agent</td>
<td>external power supply</td>
</tr>
</tbody>
</table>

- The products of the electrolysis of molten ionic compounds are predictable whereas the products of the electrolysis of an aqueous solution may be affected by factors including concentration, the nature of the electrolyte and the nature of the electrodes.
- Electrolysis can be used to produce highly reactive elements such as the strong reducing agent metals in groups 1 and 2 in the periodic table as well as chlorine and fluorine, since production by chemical reduction is not practical.
- Cations of reactive metals, including aluminium, cannot be reduced from aqueous solutions since water is a stronger oxidising agent and is preferentially reduced.
- Chlorine, sodium hydroxide and hydrogen gas can be produced industrially in the membrane cell according to the overall reaction:
  \[
  2\text{NaCl}(aq) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{NaOH}(aq) + \text{H}_2(g) + \text{Cl}_2(g)
  \]

- Aluminium can be produced industrially by the Hall–Héroult process according to the overall equation:
  \[
  2\text{Al}_2\text{O}_3(s) + 3\text{C}(s) \rightarrow 4\text{Al}(l) + 3\text{CO}_2(g)
  \]
- Electroplating is the process of coating an object with a thin film of metal deposited from an electrolytic solution by electrolysis.
- In electroplating, the object to be plated is always connected to the cathode.
- Faraday's laws can be used to calculate quantities of products produced in electrolytic cells.
- Faraday's laws can be applied to a range of problems involving quantitative calculations in electrolysis.
- Faraday's first law of electrolysis may be summarised as:
  \[
  Q = IT
  \]
  where \(Q\) is the electric charge in coulombs, \(I\) is the current in amperes and \(t\) is the time in seconds.
- Faraday's second law of electrolysis may be summarised as:
  \[
  \text{number of moles of electrons, } n(\text{electrons}) = \frac{Q}{F}
  \]
  where \(F\) is the Faraday constant representing the quantity of charge carried by 1 mole of electrons (96,500 coulombs).
- Secondary cells are electrochemical cells that can be recharged by reversing the spontaneous forward reaction through the application of a DC power source.
- The lead–acid accumulator is a secondary cell that is rechargeable; its largest use is to power transport vehicles. The discharging reaction for the operation of a lead–acid accumulator produces 12 volts and is represented by the overall equation:
  \[
  \text{PbO}_2(s) + 4\text{H}^+(aq) + \text{Pb}(s) + 2\text{SO}_4^{2−}(aq) \rightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)
  \]
  The recharging process is the reverse of the discharging process and requires approximately 14 volts of DC power to occur according to the reaction:
  \[
  2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{PbO}_2(s) + 4\text{H}^+(aq) + \text{Pb}(s) + 2\text{SO}_4^{2−}(aq)
  \]
- The nickel metal hydride rechargeable cell does not use toxic metals, stores 50% more power than NiCd cells and recharges faster. It takes advantage of the property that some metal alloys have of storing hydrogen atoms. The overall equation representing discharge is:
  \[
  \text{NiOOH}(s) + \text{MH}(s) \rightarrow \text{Ni(OH)}_2(s) + \text{M}(s)
  \]
The lithium ion cell supplies more than double the voltage of most other cells. Lithium batteries are now used extensively in portable devices because lithium's low density and high reactivity make it an excellent material for use in cells. These batteries involve carbon and cobalt oxide redox reactions.

Battery life can be affected by temperature, depth of discharge and operating voltage. These can reduce its ability to be fully recharged and affect its safe operation.

Multiple choice questions

1. Which one of the following statements about reactions in electrochemical cells and electrolytic cells is correct?
   A. Oxidation occurs at the anode of electrochemical cells and at the cathode of electrolytic cells.
   B. Electrochemical cell reactions are spontaneous whereas electrolytic cell reactions are driven by external power supplies.
   C. Electrochemical cell reactions are redox reactions whereas electrolytic cell reactions are deposition reactions.
   D. Oxidation occurs at the positive electrode in both electrochemical and electrolytic cells.

2. In an electrolytic cell, electrodes are the:
   A. ionic conductors
   B. electrical conductors
   C. ionic and electrical conductors
   D. conductors for negative ions only.

3. Which of the following best identifies the cathode in an electrolytic cell?
   A. The electrode at which anions are reduced
   B. The electrode at which no gas can be produced
   C. The electrode at which OH⁻(aq) ions are produced
   D. The electrode at which reduction occurs

4. Which one of the following occurs in the electrolysis of molten potassium bromide?
   A. Potassium is produced at the anode.
   B. Potassium ions are oxidised at the cathode.
   C. Bromine gas is produced at the cathode.
   D. Bromide ions are oxidised at the anode.

5. Which one of the following equations represents the reaction at the positive electrode in the electrolysis of molten potassium iodide?
   A. K(l) → K⁺(l) + e⁻
   B. K⁺(l) + e⁻ → K(l)
   C. 2I⁻(l) → I₂(l) + 2e⁻
   D. I₂(l) + 2e⁻ → 2I⁻(l)

6. Which of the following reactions occurs at the positive electrode when a solution of sodium sulfate, Na₂SO₄, is electrolysed using inert electrodes?
   A. Na⁺(aq) + e⁻ → Na(s)
   B. 2H₂O(l) + 2e⁻ → H₂(g) + 2OH⁻(aq)
   C. 2SO₄²⁻(aq) → 2SO₃(g) + O₂(g) + 4e⁻
   D. 2H₂O(l) → O₂(g) + 4H⁺(aq) + 4e⁻

7. A very dilute solution of sulfuric acid in water is electrolysed using platinum electrodes. The substances collected at the electrodes are:
   A. sulfur dioxide and hydrogen gas
   B. hydrogen gas and oxygen gas
   C. oxygen gas and nitrogen gas
   D. hydrogen gas and sulfur.

8. Which one of the following statements below is not true if a copper(II) sulfate solution is electrolysed using carbon electrodes?
   A. Cu²⁺(aq) ions gain electrons at the cathode because Cu²⁺(aq) ions are more easily reduced than H₂O.
   B. Water may be oxidised at the anode.
   C. Water is not reduced at the cathode.
   D. The mass of the cathode does not change.

9. In the electrolysis of molten sodium chloride using inert electrodes, which of the following occurs?
   A. Chlorine gas is produced at the cathode and oxygen gas is produced at the anode.
   B. Chlorine gas is produced at the anode and oxygen gas is produced at the cathode.
   C. Chlorine gas is produced at the cathode and sodium metal is produced at the anode.
   D. Chlorine gas is produced at the anode and sodium metal is produced at the cathode.

10. An electrolytic cell consists of two carbon electrodes and an electrolyte of aqueous sodium chloride to which phenolphthalein has been added. When an electric current is passed through the cell:
   A. bubbles of chlorine appear at the cathode
   B. bubbles of hydrogen appear at the anode
   C. a pink colour surrounds the cathode
   D. sodium metal collects at the cathode.

11. A solution contains CuCl₂, NiCl₂ and ZnCl₂, each solute being at 1 M concentration. The solution is electrolysed using graphite electrodes. Which of the following reactions takes place first at the cathode?
   A. Cu²⁺(aq) + 2e⁻ → Cu(s)
   B. Ni²⁺(aq) + 2e⁻ → Ni(s)
   C. Zn²⁺(aq) + 2e⁻ → Zn(s)
   D. 2Cl⁻(aq) → Cl₂(g) + 2e⁻

12. Which of the following reactions occurs at the anode when a solution of copper(II) sulfate is electrolysed using inert electrodes?
   A. Cu²⁺(aq) + 2e⁻ → Cu(s)
   B. 2H₂O(l) + 2e⁻ → H₂(g) + 2OH⁻(aq)
   C. 2SO₄²⁻(aq) → 2SO₃(g) + O₂(g) + 4e⁻
   D. 2H₂O(l) → O₂(g) + 4H⁺(aq) + 4e⁻
13. In an electrolytic cell with positive electrode A and negative electrode B, electrons always move towards:
   A A, and B attracts negative ions
   B A, and B attracts positive ions
   C B, and A attracts negative ions
   D B, and A attracts positive ions.

14. Consider the following standard reduction potentials:
   \[ \begin{align*}
   \text{Zn}^{2+}(aq) + 2e^- &\rightarrow \text{Zn(s)} \quad E^* = -0.76 \text{ V} \\
   2\text{H}^+(aq) + 2e^- &\rightarrow \text{H}_2(g) \quad E^* = 0.00 \text{ V} \\
   \text{Ag}^+(aq) + e^- &\rightarrow \text{Ag(s)} \quad E^* = +0.80 \text{ V} \\
   2\text{H}_2\text{O}(l) + 2e^- &\rightarrow \text{H}_2(g) + 2\text{OH}^-(aq) \quad E^* = -0.83 \text{ V}
   \end{align*} \]
   Which product would be liberated first at the cathode if a solution containing Zn(NO_3)_2 and AgNO_3 is electrolysed with platinum electrodes?
   A H_2(g)
   B Ag(s)
   C Zn(s)
   D OH^−(aq)

15. When concentrated brine solution is electrolysed in the membrane cell, the electrode products are:
   A Na(l) and Cl_2(g)
   B H_2(g) and O_2(g)
   C Na(l) and O_2(g)
   D H_2(g), Cl_2(g) and NaOH−(aq).

16. Which of the following does not usually occur during the electrolytic extraction of aluminium metal?
   A CO_2 is produced at the positive electrode.
   B Alumina is dissolved in molten cryolite, Na_3AlF_6.
   C The cathode material is consumed and replaced at frequent intervals.
   D Liquid aluminium is drawn off from the bottom of the cell.

17. Which of the following groups of substances would normally be extracted by electrolysis?
   A Iron, nickel and chromium
   B Gold, copper, silver and platinum
   C Magnesium, aluminium, sodium and chlorine
   D Oxygen, neon, argon and nitrogen

18. In the electrolytic extraction of aluminium from its oxide, a substance called cryolite is used. Which of the following best describes the function of cryolite in this process?
   A It oxidises alumina.
   B It reduces alumina.
   C It acts to absorb ore impurities from the alumina.
   D It acts as a solvent for alumina.

19. Which one of the following materials is not used in the production of aluminium metal from its ore?
   A Na_3AlF_6
   B Na_2CO_3
   C Bauxite
   D Carbon

20. What volume of chlorine (at SLC) is produced during the electrolysis of 1.00 kg of molten sodium chloride, according to the following equation?
   \[ 2\text{NaCl(l)} \rightarrow 2\text{Na(l)} + \text{Cl}_2(g) \]
   A 0.86 kg
   B 212 L
   C 383 L
   D 383 mL

21. Consider two electrolytic cells connected in series. Cell 1 contained copper(II) sulfate solution with copper electrodes and cell 2 contained copper(II) chloride solution with platinum electrodes. Current was passed for a fixed time, after which the electrodes and electrolytes in each cell were examined. The mass of the cathode in cell 2 was found to have increased in mass by 1.6 g. The anode of cell 1 would have:
   A increased by 1.6 g
   B remained unchanged in mass
   C given off oxygen gas
   D decreased in mass by 1.6 g.

22. Consider two electrolytic cells connected in series. Cell 1 contained copper(II) sulfate solution with copper electrodes and cell 2 contained copper(II) chloride solution with platinum electrodes. Current was passed for a fixed time, after which the electrodes and electrolytes in each cell were examined. The mass of the cathode in cell 2 was found to have increased in mass by 1.60 g. If no oxygen is evolved at the anode of cell 2, the volume of chlorine gas evolved when measured at SLC would be:
   A 2480 mL
   B 1250 mL
   C 625 mL
   D 310 mL.

23. Sodium perchlorate can be prepared electrolytically by the reactions:
   \[ \begin{align*}
   2\text{H}_2\text{O}(l) + 2e^- &\rightarrow \text{H}_2(g) + 2\text{OH}^-(aq) \\
   \text{Cl}^- (aq) + 8\text{OH}^-(aq) &\rightarrow \text{ClO}_4^-(aq) + 4\text{H}_2\text{O} + 8e^-
   \end{align*} \]
   What mass of sodium perchlorate could be produced in a cell that liberates 3.00 g of hydrogen gas at the cathode?
   A 45.9 g
   B 99.5 g
   C 122.5 g
   D 183.8 g

24. What volume of gaseous products is produced at 0 °C and 101.3 kPa when 18.0 g of water undergoes electrolysis?
   A 5.6 L
   B 11.2 L
   C 22.4 L
   D 33.6 L
25. If $n$ coulombs of electricity deposits 0.100 moles of silver from a solution of AgNO₃, how many coulombs are needed to deposit 0.100 moles of aluminium from a solution of Al(NO₃)₃?
   A $0.25n$
   B $0.33n$
   C $0.75n$
   D $3.00n$

26. In a secondary cell:
   A the negatively charged cathode in the discharging reaction becomes the positively charged anode in the recharging process
   B the negatively charged cathode in the discharging reaction becomes the negatively charged anode in the recharging process
   C the positively charged cathode in the discharging reaction becomes the positively charged anode in the recharging process
   D the positively charged cathode in the discharging reaction becomes the negatively charged anode in the recharging process.

27. What is important about the products in a rechargeable cell?
   A They must be gases.
   B They must be soluble in the electrolyte.
   C They must diffuse away from the electrodes.
   D They must remain in contact with the electrodes.

28. In the lead–acid car battery, the overall discharge reaction is:
   \[ \text{Pb}(s) + \text{PbO}_2(s) + 4\text{H}^+(aq) + \text{SO}_4^{2-}(aq) \rightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) \]
   During recharging, which of the following statements is correct?
   A Nickel is reduced from the +3 to +2 oxidation state.
   B Oxidation of nickel occurs from the +2 to the +3 oxidation state.
   C The reverse of the above reaction occurs at the negative electrode.
   D Oxidation occurs at the surface of the negative electrode.

### Review questions

#### Electrolysis — the process

1. In what ways are galvanic and electrolytic cells:
   (a) similar
   (b) different?

2. Why is a direct current, rather than an alternating current, used in electrolytic reactions?

3. In the electrolysis of molten sodium chloride, explain:
   (a) why electricity is conducted in the molten state but not in the solid state
   (b) why the products are formed only around the electrodes and not throughout the liquid
   (c) what causes the electric current to flow in the liquid and in the connecting wires.

4. Copy and complete the following table to summarise what happens at each electrode during electrolysis of NaCl in different forms.

<table>
<thead>
<tr>
<th>Electrolyte type</th>
<th>Reaction at Anode</th>
<th>Reaction at Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>molten salt</td>
<td>inert</td>
<td>copper</td>
</tr>
<tr>
<td>1 M aqueous salt solution</td>
<td>inert</td>
<td>copper</td>
</tr>
<tr>
<td>1 M aqueous salt solution</td>
<td>copper</td>
<td></td>
</tr>
</tbody>
</table>

5. Predict the products at the anode and cathode, write an overall equation and determine the minimum cell voltage required for the electrolysis (using carbon electrodes) of each of the following molten components.
   (a) sodium bromide
   (b) aluminium hydroxide
   (c) lead(II) chloride
   (d) magnesium chloride

6. Predict the products at the anode and cathode, write an overall equation and determine the minimum cell voltage required for the electrolysis (using carbon electrodes) of 1.0 M aqueous solutions of each of the following.
   (a) potassium hydroxide
   (b) potassium sulfate
7. Predict the products at the anode and cathode, write an overall equation and determine the minimum cell voltage required for the electrolysis of 1.0 M aqueous solutions of:
(a) copper(II) chloride
(b) copper(II) sulfate
using: (i) carbon electrodes (ii) copper electrodes.

Electrolysis in industry
8. Sodium chloride can be electrolysed to produce a number of important products. These are hydrogen, chlorine, sodium hydroxide and sodium metal.
(a) Describe and explain how the products of electrolysis of molten sodium chloride are obtained. Include the relevant equations.
(b) Describe and explain how the products of electrolysis of concentrated sodium chloride are obtained. Include the relevant equations.

9. In the production of aluminium in a Hall–Héroult cell, the anode and the cathode are made of carbon. It is found that the anode needs to be replaced every 3 weeks whereas the cathode may last up to 5 years. Explain this difference using an appropriate equation.

10. Explain, using a fully labelled diagram, how you would plate a piece of steel with nickel by electroplating.

11. In electroplating, why is the object being electroplated made the cathode?

12. In nickel-plating, what substance would you choose for:
(a) the anode
(b) the electrolyte?

13. Sketch an electrolytic cell that could be used to plate copper onto a tin keyring. On your sketch, label the:
(a) anode and cathode
(b) direction of electron flow
(c) nature of each electrode
(d) electrode polarity
(e) equations occurring at each electron.

Calculations in electrolysis — Faraday’s laws
14. How many faradays are needed to produce:
(a) 1.0 mole of copper
(b) 2.5 moles of hydrogen gas from water
(c) 15 g of aluminium
(d) 5.3 g of sodium
(e) 87 mL of oxygen gas from water at SLC?

15. Calculate:
(a) the mass of copper deposited
(b) the volume of oxygen formed at SLC during the electrolysis of aqueous copper(II) sulfate using carbon electrodes when:
   (i) a current of 1.2 A flows for 8.0 minutes
   (ii) a current of 0.75 A flows for 3.0 hours
   (iii) a current of 3.5 A flows for 2.0 hours 25 minutes
   (iv) a current of 2.4 A flows for 1.0 day.

16. Calculate the amount of time (in days) required to produce 2.00 kg of magnesium metal by the electrolysis of molten magnesium chloride, MgCl₂, using a current of 45.0 A.

17. A metal M forms a chloride with the formula MCl₂. Crystals of MCl₂ were placed in a crucible and heated. The molten chloride was then electrolysed using carbon electrodes. The ammeter in the circuit read 0.250 A and the current was passed for 4 hours 56.0 minutes. The mass of M deposited was 1.28 g.
(a) Write an equation for the reaction at the cathode.
(b) Calculate the number of moles of M produced.
(c) Determine the atomic mass of M.
(d) Use your periodic table to suggest a metal that M could be.
(e) Draw a diagram of the apparatus suitable for this experiment.

18. Chromium chloride is electrolysed using chromium electrodes. A current of 0.200 A flows for 1447 seconds. The increase in the mass of the cathode is 0.0520 g.
(a) How many coulombs of electricity are used?
(b) How many moles of chromium are liberated?
(c) How many moles of electrons are transferred?
(d) What is the charge on the chromium ion?

19. When a current of 10.0 A was passed through a concentrated solution of sodium chloride using carbon electrodes, 2.80 L of chlorine (at SLC) was collected. How long (in minutes) did the electrolysis take?

20. A current of 4.25 A is passed through molten Al₂O₃ for 13.5 hours.
(a) How many grams of aluminium would be produced?
(b) What volume of oxygen, at 152 kPa (1.50 atm) and 290 °C, would be evolved?

21. Calculate the time taken to deposit gold from a solution of gold(I) cyanide to a thickness of 0.0100 mm onto a copper disc that has a diameter of 10.0 mm and a thickness of 5.00 mm if a current of 0.750 A is used. (The density of gold is 19.3 g cm⁻³.)
22. (a) What volumes of hydrogen gas, $\text{H}_2$, and oxygen gas, $\text{O}_2$, are produced from the electrolysis of water by a current of 2.50 A in 15.0 minutes at SLC?
(b) Identify the reactions occurring at the electrodes in the reaction in (a).

23. A solution containing a $3^+$ metal ion is electrolysed by a current of 2.00 A for 25.0 minutes. What is the identity of the metal if 1.19 g of the metal was deposited on the cathode?

24. How many electrons are required to deposit 1.00 g of copper from copper($II$) sulfate solution?

25. Sir Humphry Davy discovered sodium by electrolysis of molten sodium hydroxide. How long (in minutes) must a current of 1.5 A flow to produce 1.0 gram of sodium?

26. A Hall–Heroult cell is an electrolytic cell in which molten alumina, $\text{Al}_2\text{O}_3$, is electrolysed to produce aluminium. The overall reaction may be written:

$$4\text{Al}^{3+}(\text{l}) + 6\text{O}^{2-}(\text{l}) + 3\text{C(s)} \rightarrow 4\text{Al}(\text{l}) + 3\text{CO}_2(\text{g})$$

A typical Hall–Heroult cell uses a current of $1.70 \times 10^5$ A. Assuming 98% efficiency, calculate the following for a 24-hour period:
(a) the mass of aluminium produced
(b) the volume of carbon dioxide formed at SLC.

27. A given quantity of electricity is passed through two cells containing solutions of silver nitrate and tin($II$) chloride respectively. What mass of tin is deposited in one cell if 2.00 g of silver is deposited in the other cell?

28. What current is needed to deposit 0.65 g of silver onto a metal spoon in 1.0 hour?

29. A home renovator wants to chrome-plate her kitchen tap so that a layer of chromium 0.150 mm thick is evenly plated over the tap. The total surface area of the tap is 35.0 cm$^2$. Given that the density of chromium is 7.20 g cm$^{-3}$, calculate the time (in hours) that the tap should be left in the electrolytic bath of chromium($III$) nitrate if the bath has a current of 4.55 A passing through it.

30. Why are lead–acid accumulators often referred to as storage batteries?

31. For a lead–acid storage cell:
(a) What is the standard cell potential?
(b) What is the battery potential, assuming it is composed of six lead–acid storage cells?
(c) Describe the composition of the anode, cathode and electrolyte when it is fully discharged.

32. The Edison cell is a 1.3-volt storage battery that can be recharged, even after long periods of being left uncharged. Its electrolyte is 21% potassium hydroxide solution and the reaction on discharge is:

$$\text{Fe(s)} + 2\text{NiO(OH)(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Fe(OH)}_2(\text{s}) + 2\text{Ni(OH)}_2(\text{s})$$

(a) Outline two uses for which this type of cell would be ideal.
(b) Give electrode reactions during:
(ii) discharging
(iii) recharging.
(c) What materials would be used for the electrodes?
(d) In the discharge process, which electrode is the anode and which is the cathode?
(e) In the recharge process, which electrode is the anode and which is the cathode?

33. The market for lithium batteries is continually increasing in our energy-hungry society. Applications of this technology extend from tiny cells used in medical implants, to laptops, mobile phones and military devices.
(a) What properties of lithium make it so useful for cells?
(b) Discuss the chemistry involved in the operation of a lithium cell compared with the operation of a nickel metal hydride cell.
Exam practice questions

In a chemistry examination, you will be required to answer a number of multiple choice and extended response questions.

Extended response questions

1. An aqueous solution of NiBr₂ is electrolysed using inert electrodes.
   (a) Sketch the cell showing:
       (i) the direction of current flow in the external circuit and through the electrolyte
       (ii) the cathode and anode, and their polarity.
   2 marks

   (b) Write half-equations for the expected reactions at each electrode, and then write the overall equation.
   2 marks

   (c) Calculate the minimum voltage needed to electrolyse the solution under standard conditions (SLC).
   1 mark

   (d) Explain how the products of electrolysis would differ if nickel electrodes were used.
   2 marks

2. After Millikan showed that the charge on an electron was $1.6 \times 10^{-19}$ coulomb, electrolytic reactions were used to obtain accurate estimates of the Avogadro constant. Consider a current of 0.10 A flowing through an electrolytic solution to produce a deposit of 0.10 g of copper.
   (a) Find the charge passing through the cell if the time taken for the deposit was 50 minutes and 40 seconds.
   1 mark

   (b) Calculate the amount of copper produced.
   1 mark

   (c) Write the equation for the reaction and hence calculate the number of moles of electrons consumed.
   2 marks

   (d) Calculate the charge on 1 mole of electrons.
   2 marks

   (e) Calculate the Avogadro constant, given that the charge on an electron is $1.6 \times 10^{-19}$ coulombs.
   1 mark

3. What mass (in kg) of chlorine gas is produced in 1.00 hours in an electrolytic cell using a concentrated NaCl electrolyte, given that the current is $1.40 \times 10^3$ A and the cell’s efficiency is 90%?
   5 marks