7 Production of chemicals by electrolysis and Rechargeable batteries

7.1 Overview

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7.1.1 Introduction

Chlorine is one of the most widely used chemicals in the world. It is perhaps best known for its use as disinfectant in large public swimming pools. Upon addition to the pool water, chlorine reacts to form hypochlorite ions which serve as a powerful disinfectant. But chlorine has many more uses — it is used in the manufacture of organic compounds, plastics, bleach and chlorinated lime.

Chlorine is made on a large scale by the process of electrolysis. Electrolysis is also used to make sodium hydroxide and aluminium, and is central to electroplating and the production of extremely pure copper.

This topic introduces the process of electrolysis and how the variables involved can alter the nature of the products produced. Faraday’s Laws can be then applied to make quantitative predictions concerning electrolytic cells.

You will use your prior knowledge of basic redox concepts. Features of galvanic cells that you learnt about in topic 3 will be critical to your understanding of electrolytic cells. Furthermore, you will make extensive use of the electrochemical series as a tool for predicting electrode reactions and of your skills in stoichiometry.

7.1.2 What you will learn

KEY KNOWLEDGE
In completing this topic, you will investigate:
Production of chemicals by electrolysis
  • electrolysis of molten liquids and aqueous solutions using different electrodes
• the general operating principles of commercial electrolytic cells, including basic structural features and selection of suitable electrolyte (molten or aqueous) and electrode (inert or reactive) materials to obtain desired products (no specific cell is required)
• the use of the electrochemical series to explain or predict the products of an electrolysis, including identification of species that are preferentially discharged, balanced half-equations, a balanced ionic equation for the overall cell reaction, and states
• the comparison of an electrolytic cell with a galvanic cell with reference to the energy transformations involved and basic structural features and processes
• the application of stoichiometry and Faraday’s Laws to determine amounts of product, current or time for a particular electrolytic process.

Rechargeable batteries
• the operation of rechargeable batteries (secondary cells) with reference to discharging as a galvanic cell and recharging as an electrolytic cell, including the redox principles (redox reactions and polarity of electrodes) and the factors affecting battery life with reference to components and temperature (no specific battery is required).


PRACTICAL WORK AND INVESTIGATIONS
Practical work is a central component of learning and assessment. Experiments and investigations, supported by a Practical investigation logbook and Teacher-led videos, are included in this topic to provide opportunities to undertake investigations and communicate findings.

Resources

Digital documents
Key science skills (doc-30903)
Key terms glossary — Topic 7 (doc-31409)
Practical investigation logbook (doc-31410)

To access key concept summaries and past VCAA exam questions download and print the studyON: Revision and practice exam question booklet (doc-31411).

7.2 What is electrolysis?

KEY CONCEPT
• Electrolysis of molten liquids and aqueous solutions using different electrodes

7.2.1 The process of electrolysis
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:

$$\text{Cu}^{2+} (aq) + 2e^- \rightleftharpoons \text{Cu} (s) \quad E^0 = +0.34 \text{ V}$$

$$\text{Zn}^{2+} (aq) + 2e^- \rightleftharpoons \text{Zn} (s) \quad E^0 = -0.76 \text{ V}$$
Because the $E^0$ value for the Cu$^{2+}$/Cu redox pair is greater than the $E^0$ value for the Zn$^{2+}$/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. This reaction is the reverse of the one that produces energy, so 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 referred to as DC (direct current).

The external power source supplies the electrons. Electrons flow from the external power source to the negative electrode (the cathode), which is the site of reduction. Electrons are withdrawn by the power source from the positive electrode (the anode), which is the site of oxidation. Cations are attracted to the cathode and anions are attracted to the anode. The cations gain electrons from the cathode and the anions give up electrons to the anode.

**Figure 7.2** An electrolytic cell

**Resources**

Video eLesson Features of electrolytic cells (med-0439)

### 7.2.2 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 can 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, \( \text{Na}^+ \), and chloride ions, \( \text{Cl}^- \), are held tightly together. Heating the solid causes the ions in the crystal to separate and 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.

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

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

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

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

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

**SAMPLE PROBLEM 1**

**a.** Write the equations for the reactions at each electrode when pure molten magnesium chloride undergoes electrolysis.

**b.** Write the overall equation for this reaction.

**THINK**

**WRITE**

**a.** In molten magnesium chloride there are mobile \( \text{Mg}^{2+} \) and \( \text{Cl}^- \) ions. These are the only possible reactants for electrolysis.

The \( \text{Mg}^{2+} \) ions will move to the negative electrode (the cathode) where they will accept electrons and be reduced.

\[
\text{Mg}^{2+}(l) + 2e^- \rightarrow \text{Mg}(l)
\]

The \( \text{Cl}^- \) ions will move to the positive electrode (the anode) where they will give up electrons and be oxidised.

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

**b.** Obtain the overall equation by adding the half equations together, making sure that the electrons cancel out.

**TIP**: Make sure that you use the correct symbols of state for magnesium. It is liquid (not aqueous) under these conditions.

**PRACTICE PROBLEM 1**

**a.** Write the equations for the reactions at each electrode when pure molten potassium iodide undergoes electrolysis.

**b.** Write the overall equation for this reaction.
7.2.3 Electrolysis of water

When a current is applied via two electrodes in pure water, nothing happens. There is no current flow and no electrolysis. But, if an electrolyte such as H$_2$SO$_4$ or KNO$_3$ 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.

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

At the anode, water is oxidised to form oxygen.

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

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.

\[
6\text{H}_2\text{O(l)} \rightarrow 2\text{H}_2(g) + \text{O}_2(g) + 4\text{H}^+(aq) + 4\text{OH}^-(aq)
\]

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

\[
4\text{H}^+(aq) + 4\text{OH}^-(aq) \rightarrow 4\text{H}_2\text{O(l)}
\]

These do not need to be included in the final overall equation.

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

7.2.4 Electrolysis of aqueous solutions

In the electrolysis of water, it is necessary to add a small amount of electrolyte before electrical conduction can take place. This is done at a very low concentration and, as a result, water is effectively the only substance that can react to the passing of the electrical current. In the electrolysis of molten sodium chloride in section 7.2.3, there was also only one reaction possible at each electrode.

More complicated electrolysis systems involve situations where more than one reaction is possible at each electrode. The next two examples illustrate this. Note that in the second example, the choice of the electrode itself may also be a significant factor in the reactions that take place.

Electrolysis of dilute sodium chloride solution with inert electrodes

In many electrolysis reactions, inert electrodes are used. These are electrodes that do not affect the reactions taking place on their surfaces, and which conduct a current but do not tend to go into solutions as ions. They are usually carbon, in the form of graphite, or platinum, which is much more expensive. As shown in figure 7.5, there is a choice of reactants at each electrode when dilute sodium chloride is electrolysed.
At the cathode, sodium ions are present and the cathode is in contact with water molecules from the solvent. It is observed that a gas is produced, which proves to be hydrogen. If a few drops of phenolphthalein indicator are added to the region around the cathode it turns pink. From these observations we can infer that OH\(^{-}\) ions are also produced.

The production of H\(_2\) and OH\(^{-}\) is consistent with the water being reduced in preference to the Na\(^{+}\) ions, according to:

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

At the anode, a choice between water and chloride ions is possible. The observed evolution of oxygen gas, together with a few drops of phenolphthalein remaining clear, support the conclusion that water is once again reacting at this electrode, but this time it is being oxidised. This is due to the relative reducing strength of water and chlorine and is discussed in section 7.3.

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

**Electrolysis of dilute sodium chloride solution with copper electrodes**

If the previous experiment is repeated using copper electrodes instead of inert electrodes, the results change. This illustrates that the choice of electrodes has an effect on the nature of the products of an electrolysis.

This time the equations occurring at each electrode are:

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

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

It can be seen that Cu\(^{2+}\) ions are produced instead of O\(_2\) gas at the anode. This is due to the relative reducing strength and is discussed in section 7.3.

**SAMPLE PROBLEM 2**

What are the possible reactants around each electrode when a dilute copper sulfate solution is electrolysed?

Note that under conditions of dilute electrolysis in aqueous solutions, ions such as sulfate and nitrate are typically inert.

**THINK**

1. Identify the constituents of the electrolyte.
2. Around the cathode reduction occurs and Cu\(^{2+}\) ions and H\(_2\)O molecules can potentially be reduced.
3. Around the anode oxidation occurs and SO\(_4^{2-}\) ions and H\(_2\)O molecules can potentially be oxidised. The SO\(_4^{2-}\) ions can be ignored.

**WRITE**

Cu\(^{2+}\); SO\(_4^{2-}\) and H\(_2\)O

Possible reactants cathode: Cu\(^{2+}\) ions and H\(_2\)O molecules

Possible reactants anode: H\(_2\)O
PRACTICE PROBLEM 2
What are the possible reactants around each electrode when a dilute potassium nitrate solution is electrolysed?

7.2 EXERCISE
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1. Predict the products that are formed when molten potassium chloride (KCl) undergoes electrolysis.
2. Give two observations that would be noted during the electrolysis of dilute sodium chloride with copper electrodes.
3. Explain how the addition of a small amount of KNO₃ allows water to conduct electricity and hence undergo electrolysis.
4. With reference to figure 7.4, and also to the equation for the decomposition of water, predict which side of the apparatus collects hydrogen gas and which collects oxygen gas.
5. Glass is an inert substance under virtually all conditions. Explain why glass cannot be used as an electrode material.
6. (a) Explain why the cathode has a negative charge in an electrolysis cell.
   (b) Explain why the anode has a positive charge in an electrolytic cell.
7. 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.
8. Give an example of an electrolysis reaction where the nature of the electrodes influences the products produced.
9. During the electrolysis of molten lithium iodide, what product will form around the cathode and what will form around the anode? Explain.
10. Answer the following questions for electrolysis of molten potassium bromide.
    (a) Write the equation for the reaction occurring at the cathode.
    (b) State the sign of the cathode.
    (c) Write the equation for the reaction occurring at the anode.
    (d) State the sign of the anode.
    (e) Write the overall ionic equation for this electrolysis.

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7.3 Predicting reactions that occur during electrolysis

KEY CONCEPT
- The use of the electrochemical series to explain or predict the products of an electrolysis, including identification of species that are preferentially discharged, balanced half-equations, a balanced ionic equation for the overall cell reaction, and states

7.3.1 Using the electrochemical series
When a molten salt is electrolysed, the products are predictable. However, as shown in subtopic 7.2, 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. From the examples seen so far, when there is a choice of two possible oxidising agents or reducing agents, one of these is preferentially reacted. As explained in topic 4, oxidising agents and reducing agents have different strengths, which can be used to produce an electrochemical series. As we shall now see, the electrochemical series also plays an important part in the redox reactions that occur during electrolysis. It can be used to help predict the products of electrolysis when multiple reactions are possible.

Predicting the products of electrolysis

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 $E^0$.
3. Circle the species present in the electrolytic cell that could participate.
4. Select the oxidising agent with the highest $E^0$ (the strongest oxidising agent). This will be reduced at the cathode, because it requires less energy for reduction than an oxidising agent with a lower $E^0$.
5. Select the reducing agent with the lowest $E^0$ (the strongest reducing agent). This will be oxidised at the anode, because it requires less energy for oxidation than a reducing agent with a higher $E^0$.
6. Write the overall equation by combining the relevant half-equations.
7. Determine the minimum voltage required to achieve the reaction by subtracting the $E^0$ of the reducing agent from the $E^0$ of the oxidising agent.

$$\text{minimum voltage required} = E^0_{\text{oxidising agent}} - E^0_{\text{reducing agent}}$$

The electrolysis of dilute potassium iodide is shown in figure 7.8.

1. The species present in the cell are $K^+$, $I^-$ and $H_2O$.
2. The possible half-equations for these species, in descending order of $E^0$ are listed using table 2 of the VCE Chemistry Data Book.
3. The species present in the electrolytic cell that could participate are then circled.

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$  \hspace{1cm} $E^0 = +1.23 \text{ V}$

$I_2(s) + 2e^- \rightarrow 2I^-(aq)$  \hspace{1cm} $E^0 = +0.54 \text{ V}$

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$  \hspace{1cm} $E^0 = -0.83 \text{ V}$

$K^+(aq) + e^- \rightarrow K(s)$  \hspace{1cm} $E^0 = -2.93 \text{ V}$
4. Recall the acronym OILRIG (oxidation is loss, reduction is gain) and that reduction occurs at the cathode, so there are two possible reactions in this cell. The oxidising agent with the highest $E^0$ value (the strongest oxidising agent) requires the least energy for reduction and is reduced at the cathode. So, water reacts in preference to potassium ions at the cathode.

Cathode: $2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$ \hspace{1cm} $E^0 = -0.83 \text{ V}$

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

5. Oxidation occurs at the anode, so there are two possible reactions. The reducing agent with the lowest $E^0$ value (the strongest reducing agent) requires the least energy for oxidation and is oxidised at the anode. Thus, iodide ions react in preference to water molecules at the anode.

Anode: $2\text{I}^-(aq) \rightarrow \text{I}_2(s) + 2e^- \hspace{1cm} E^0 = +0.54 \text{ V}$

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

6. The overall electrolytic cell reaction would be:

$$2\text{H}_2\text{O}(l) + 2\text{I}^-(aq) \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq) + \text{I}_2(s)$$

7. Determine the minimum voltage required 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 7.1.

### TABLE 7.1 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$_2$(l) – a melt</td>
<td>Pb(s)</td>
<td>Br$_2$(g)</td>
</tr>
<tr>
<td>NaCl(l) – 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) deposited</td>
<td>Cu(s) dissolves to form Cu$^{2+}$ ions</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>
SAMPLE PROBLEM 3

A dilute solution containing tin(II) chloride and copper sulfate is electrolysed using inert electrodes. Predict the products that will form at each electrode and write the relevant half-equations. Use these to write the overall equation and determine the minimum voltage required to achieve the reaction.

THINK
1. Identify the constituents of the solution.
2. From table 2 (Electrochemical series) of the VCE Chemistry Data book, copy the half-equations for the species in descending order of standard electrode potentials. \( \text{SO}_4^{2-} \) ions will not react.

TIP: When using the electrochemical series, be careful with Sn\(^{2+} \) because it occurs in more than one place. (The same applies to Fe\(^{2+} \).)

3. Circle the species present in the electrolytic cell that could participate.

4. At the cathode, the strongest oxidising agent (highest \( E^0 \)) undergoes reduction. Copper metal will form.

5. At the anode, the strongest reducing agent (lowest \( E^0 \)) undergoes oxidation. \( \text{Sn}^{4+} \) ions will form.

6. Write the overall equation by combining the relevant half-equations.

7. Determine the minimum voltage required by subtracting the \( E^0 \) of the reducing agent from the \( E^0 \) of the oxidising agent.

WRITE
Sn\(^{2+} \), Cl\(^- \), Cu\(^{2+} \), \( \text{SO}_4^{2-} \) and \( \text{H}_2\text{O} \) molecules

\[
\begin{align*}
\text{Cl}_2(g) + 2e^- & \rightleftharpoons 2\text{Cl}^-(aq) \quad E^0 = +1.36 \text{ V} \\
\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- & \rightleftharpoons 2\text{H}_2\text{O}(l) \quad E^0 = +1.23 \text{ V} \\
\text{Cu}^{2+}(aq) + 2e^- & \rightleftharpoons \text{Cu}(s) \quad E^0 = +0.34 \text{ V} \\
\text{Sn}^{4+}(aq) + 2e^- & \rightleftharpoons \text{Sn}^{2+}(aq) \quad E^0 = +0.15 \text{ V} \\
\text{Sn}^{2+}(aq) + 2e^- & \rightleftharpoons \text{Sn}(s) \quad E^0 = -0.14 \text{ V} \\
2\text{H}_2\text{O}(l)+2e^- & \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-(aq) \quad E^0 = -0.83 \text{ V}
\end{align*}
\]

Cathode: \( \text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \quad E^0 = +0.34 \text{ V} \)

Anode: \( \text{Sn}^{2+}(aq) \rightarrow \text{Sn}^{4+}(aq) + 2e^- \quad E^0 = +0.15 \text{ V} \)

\( \text{Cu}^{2+}(aq) + \text{Sn}^{2+}(aq) \rightarrow \text{Cu}(s) + \text{Sn}^{4+} \)

Minimum voltage required = \( +0.34 - 0.15 = +0.19 \text{ V} \)

PRACTICE PROBLEM 3

A dilute solution containing silver nitrate and cobalt(II) chloride is electrolysed using inert electrodes. Predict the products that will form at each electrode and write the relevant half-equations. Use these to write the overall equation and determine the minimum voltage required to achieve the reaction.
TIP: The electrochemical series is written as a series of reversible reduction reactions. Don’t forget to reverse these equations when writing an oxidation reaction. When you have decided whether an oxidation or reduction equation is required remember to use only a single arrow in your equation.

7.3.2 Factors affecting electrolysis of 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 can 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 can be written.

The effect of concentration

The electrochemical series (see table 3.2 in section 3.4.1 or Table 2 of the VCE Chemistry Data book) is a useful tool for predicting the products of an electrolysis reaction. However, it must be remembered 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. For example, in the electrolysis of dilute sodium chloride reduction occurs at the cathode. The possible reactions are:

Cathode: \( 2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \quad E^0 = -0.83 \text{ V} \)

\( Na^+(aq) + e^- \rightleftharpoons Na(l) \quad E^0 = -2.71 \text{ V} \)

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:

Anode: \( Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \quad E^0 = +1.36 \text{ V} \)

\( O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l) \quad E^0 = +1.23 \text{ V} \)

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

The overall equation is:

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

However, at higher concentrations of chloride ions (> 6 M), the discharge of chlorine becomes more favourable. The reduction of water, rather than of sodium ions, still occurs at the cathode at higher concentrations of sodium ions. Therefore, the electrolysis of dilute sodium chloride 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 \( E^0 \) values for the following reactions are examined.

\( Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \quad E^0 = 1.36 \text{ V} \)

\( O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l) \quad E^0 = 1.23 \text{ V} \)

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 H\(_2\)O and Na\(^+\) ions is too large. Thus, when concentrated sodium chloride (>6 M) 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 is electrolysed instead of concentrated sodium chloride solution, the results are different. At the anode, chlorine gas is evolved in both cells, because 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 previously. In the copper chloride cell, two reactions are possible at the cathode.

\[
\text{Cathode: } \text{Cu}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cu}(s) \quad E^0 = +0.34 \text{ V}
\]

\[
2\text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-(aq) \quad E^0 = -0.83 \text{ V}
\]

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 results in the production of oxygen gas or chlorine gas (depending on the concentration of the solution; see table 7.1) at the anode. However, if copper electrodes are used, copper(II) ions are produced at the anode because the electrode itself acts as a stronger reducing agent than either water molecules or chloride ions. The copper anode dissolves to form Cu\(^{2+}\) ions.

\[
\text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^-(aq) \quad E^0 = +1.36
\]

\[
\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(l) \quad E^0 = +1.23 \text{ V}
\]

\[
\text{Cu}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cu}(s) \quad E^0 = +0.34 \text{ V}
\]
SAMPLE PROBLEM 4

A solution of copper(II) sulfate is electrolysed using nickel electrodes. Write the half-equations for the reaction occurring at each electrode. Use these to write the overall equation and determine the minimum voltage required to achieve the reaction.

WRITE

1. Identify the constituents of the solution. $\text{Cu}^{2+}, \text{SO}_4^{2-}$ and $\text{H}_2\text{O}$ molecules. Ni from the electrode might react as well.

2. From table 2 (Electrochemical series) of the VCE Chemistry Data book, copy the half-equations for the species in descending $E^0$ order.

3. Circle the species present in the electrolytic cell that could participate.

4. At the cathode, the strongest oxidising agent (highest $E^0$) undergoes reduction.

5. Identify the strongest reducing agent and write the equation for the anode.

6. Write overall equation by combining the relevant half-equations.

7. Determine the minimum voltage required by subtracting the $E^0$ of the reducing agent from the $E^0$ of the oxidising agent.

PRACTICE PROBLEM 4

A solution of lead(II) nitrate is electrolysed using iron electrodes. Write the half-equations for the reaction occurring at each electrode. Use these to write the overall equation and determine the minimum voltage required to achieve the reaction.

Resources

Video eLesson  Predicting the products of electrolysis (med-0440)

Digital documents  Experiment 7.1 Electrolysis of aqueous solutions (doc-31264)
          Experiment 7.2 Factors affecting electrolysis (student design) (doc-31265)

Teacher-led video  Experiment 7.1 Electrolysis of aqueous solutions (tlvd-0749)
7.3 EXERCISE

To answer questions online and to receive immediate feedback and sample responses for every question go to your learnON title at www.jacplus.com.au.

1. Write the equations for the reaction at each electrode when a 1 M solution of ZnBr$_2$ undergoes electrolysis. Use these equations to write the overall equation for this reaction.

2. (a) Write the equations for the reaction at each electrode when a 1 M solution of hydrochloric acid is electrolysed using silver electrodes. Use these equations to write the overall equation for this reaction.
   (b) Why is it not possible to electrolyse this solution with nickel electrodes? Remember from Unit 2 that hydrochloric acid is a strong acid and a 1 M solution will therefore consist almost entirely of H$^+$ ions and Cl$^-$ ions.

3. Write the half-equation that occurs at the cathode and the anode when a dilute solution of Na$_2$SO$_4$ is electrolysed using inert electrodes.

4. Predict the products and the minimum cell voltage required for the electrolysis of a 1 M solution of aluminium chloride.

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

6. 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 question 6a are used up, what will be the next product observed at the cathode?
   (c) If the electrolysis is continued further until the product from question 6b is observed to stop forming, what will be the third product formed at the cathode?

7. Write the half-equations and overall ionic equations for the electrolysis of:
   (a) molten nickel iodide (NiI$_2$)
   (b) 1 M nickel iodide solution.

8. Magnesium can 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 can 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.

9. A solution containing both Zn(NO$_3$)$_2$ and AgNO$_3$, with both at 1 M concentration, undergoes electrolysis using platinum electrodes. If this electrolysis is allowed to proceed for a long time, in what order will the products at the cathode appear?

10. A dilute solution of copper sulfate is electrolysed using platinum electrodes.
    (a) Write the half-equations for the reactions at each electrode.
    (b) How will the concentration of Cu$^{2+}$ ions change during this process?
    (c) If the platinum electrodes are replaced by copper electrodes:
        (i) Write the half-equations for the reactions that now occur at each electrode.
        (ii) How will the concentration of Cu$^{2+}$ ions change during this time?

11. Sometimes reaction products from an electrolysis reaction may be different to those predicted. How might this happen?

12. Why is it not possible to electrolyse a solution containing tin(II) chloride and iron(III) chloride?
7.4 Commercial applications of electrolysis

**KEY CONCEPT**
- The general operating principles of commercial electrolytic cells, including basic structural features and selection of suitable electrolyte (molten or aqueous) and electrode (inert or reactive) materials to obtain desired products (no specific cell is required)

**TIP:** Some examples of commercial electrolytic cells are provided in this subtopic. Although you are not required to know the details of any specific cell, you should examine these examples and make sure that you understand the principles behind their operation. It is expected that you should be able to apply these principles in an examination, rather than just restating facts that you have learnt.

7.4.1 Producing aluminium

Although aluminium is the most abundant metallic element in the Earth’s crust, it was difficult to extract before 1886. 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. One hundred and thirty years ago, only the wealthy could afford aluminium. Napoleon III of France was famous for serving food to special guests at banquets on aluminium plates, while ordinary guests were served food on plates made from gold! The aluminium extraction breakthrough came in 1886 with the development of what we now call the Hall–Héroult cell.

The Hall–Héroult cell

Paul Héroult, a French scientist, and Charles Hall, an American inventor and chemist, almost simultaneously filed patent applications for the industrial electrolytic production of aluminium, despite working completely independently of each other. 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 64 million tonnes per year today.

The industrial production of aluminium occurs in a Hall–Héroult cell (see figure 7.11) and involves electrolysis of alumina that is dissolved in molten cryolite (Na$_3$AlF$_6$). 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 suspended above the cell and partially immersed in the electrolyte act as anodes, while the carbon lining of the cell acts as the cathode.

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.

\[
\begin{align*}
2\text{H}_2\text{O}(l) + 2e^- & \rightarrow \text{H}_2(g) + 2\text{OH}^- (aq) & E^0 &= -0.83 \text{ V} \\
\text{Al}^{3+} (aq) + 3e^- & \rightarrow \text{Al}(s) & E^0 &= -1.67 \text{ V}
\end{align*}
\]

Cryolite, Na$_3$AlF$_6$, acts as a solvent and an electrolyte 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.

**FIGURE 7.11** Schematic diagram of a cross-section of a Hall–Héroult cell for the electrolytic production of aluminium

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, Al\(_2\)O\(_3\), is fed into the electrolyte at regular intervals where it dissolves, forming aluminium ions, Al\(^{3+}\), and oxide ions, 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.

\[
\text{Anode: } 2\text{O}^{2-}(l) \rightarrow \text{O}_2(g) + 4e^- \\
\text{O}_2(g) + C(s) \rightarrow \text{CO}_2(g)
\]

The overall reaction at the anode can therefore be written as:

\[
\text{Anode: } C(s) + 2\text{O}^{2-}(l) \rightarrow \text{CO}_2(g) + 4e^-
\]

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 three 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.

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

The density difference between cryolite and the newly formed molten aluminium allows the aluminium to settle at the bottom of the cell where it is regularly drained out. After draining, the molten aluminium can be cast.

The overall reaction for the electrolytic production of aluminium by electrolysis can be represented as:

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

Carbon dioxide is the main gas produced in this process. Other gases produced 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 falls to the bottom of the cell instead of dissolving (because it is denser than molten aluminium). There, 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 electrical resistance to the flow of this current generates enough heat to keep the electrolyte in a liquid state.

7.4.2 The industrial electrolysis of brine

Chlorine gas, hydrogen gas and sodium hydroxide are three important industrial chemicals. They can 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. This is done 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 hydroxide ions to pass from one electrode half-cell to the other but does not allow chloride 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 and hydrogen gas, which is evolved at the cathode. Chlorine gas is produced at the anode. The relevant equations are:

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

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

As with all electrolytic cells, the products are prevented from coming into contact with each other. The overall reaction for the production of chlorine via the membrane cell process is:

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

Electroplating is the process of coating an object in a metal. Inexpensive silver-plated jewellery can be produced through electroplating. ‘Gold’ rings that turn fingers 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. These include:

- the carefully controlled concentration of the cations to be reduced in the plating solution. Unwanted side reactions must be avoided.
- the careful consideration of the type and concentration of electrolyte
- the solution, which must contain compounds to control the acidity and increase the conductivity
- the compounds, some of which make the metal coating brighter or smoother
- the shape of the anode, which must often be shaped like the object at the cathode to achieve an even metal coating.

Silver-plating

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

Cathode: \[ \text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s) \]
At the same time, silver atoms at the anode form silver ions.

Anode: Ag(s) → Ag⁺(aq) + e⁻

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. Therefore, the silver metal 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.

**FIGURE 7.14 Silver-plating mechanism for cutlery**

![Silver-plating mechanism diagram]

**Resources**

- **Interactivity** Electroplating simulation (int-1258)
- **Digital documents** Experiment 7.3 Electroplating (doc-31266)
- **Teacher-led video** Experiment 7.3 Electroplating (tlvd-0751)

### 7.4 EXERCISES

To answer questions online and to receive immediate feedback and sample responses for every question go to your learnON title at www.jacplus.com.au.

1. List all the products produced from the commercial electrolysis of a brine solution using a membrane cell.
2. Why is it important that the membrane used in a membrane cell be impervious to OH⁻ ions?
3. Aluminium metal cannot be produced by the electrolysis of an aqueous solution of its ions. List two other metals that also cannot be produced this way.
4. (a) What is the main advantage of the electrolytic production of aluminium from alumina, Al₂O₃, dissolved in cryolite rather than from straight molten alumina?
   (b) Why can’t a solution of alumina dissolved in water at normal temperatures be used instead?
5. Membrane cells operate using a concentrated solution of sodium chloride. Explain what would happen if this solution was allowed to become diluted.
6. The addition of cryolite, Na₃AlF₆, in the Hall–Héroult process introduces Na⁺(l) and F⁻(l) into the mixture. Why is there no issue with contamination?
7. In the production of aluminium in a Hall–Héroult cell, the cathode and anode are made of carbon. The anode needs to be replaced every three weeks whereas the cathode can last up to five years. Explain this difference using an appropriate equation.
8. Using a fully labelled diagram, explain how you would plate a piece of lead with nickel by electroplating.
9. In electroplating, why is the object being electroplated made the cathode?
10. In nickel-plating, what substance would you choose for:
    (a) the anode?
    (b) the electrolyte?
### 7.5 Comparing galvanic and electrolytic cells

#### KEY CONCEPT
- The comparison of an electrolytic cell with a galvanic cell with reference to the energy transformations involved and basic structural features and processes

#### 7.5.1 Similarities and differences between galvanic and electrolytic cells

Consider the following redox half-equations:

- \[
  \text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \quad E^0 = +0.34 \text{ V}
  \]
  \[
  \text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s) \quad E^0 = -0.76 \text{ V}
  \]

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. However, if 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 are needed to force this non-spontaneous reaction to occur.

In both galvanic and electrolytic cells, oxidation occurs at the anode and reduction occurs at the cathode. However, in an electrolytic cell, the cathode is negative because the external DC source forces electrons onto it. Therefore, zinc ions, \(\text{Zn}^{2+}\), are attracted to the cathode where they pick up electrons to form zinc atoms.

The anode in an electrolytic cell is positive because the DC source withdraws electrons from it. Electrons are supplied to the positive anode by the oxidation of the copper electrode itself.

In an electrolytic cell, the polarity of the electrodes is determined by the external DC source. In contrast, the polarity of the electrodes in a galvanic cell develops due to the spontaneous redox reaction occurring within the cell itself. Table 7.2 summarises the major similarities and differences between galvanic and electrolytic cells.
**TABLE 7.2** Comparison of 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>

**FIGURE 7.15** Comparison of zinc–copper half-cells in electrochemical and electrolytic reactions

(a) Galvanic cell showing fully labelled components, half-equations and overall equation. (b) Electrolytic cell showing fully labelled components, half-equations and overall equation.

Electrolysis is most often carried out in a single container (see figure 7.16) and almost never in double containers connected with a salt bridge (see figure 7.15). This is possible because the reactants in an electrolytic cell do not react spontaneously and can be mixed. Reaction only occurs once electrical energy is supplied to bring about the non-spontaneous reactions of the electrolysis process.
FIGURE 7.16 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.

\[ \text{Zn}^{2+} (aq) + 2e^- \rightarrow \text{Zn}(s) \]  
reduction  
cathode  
(–)

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

movement of anions  
movement of cations  

Resources

- **Resources** Comparing galvanic and electrolytic cells (int-1257)
- **Interactivity**: Introduction to electrolysis

7.5 EXERCISE
To answer questions online and to receive immediate feedback and sample responses for every question go to your learnON title at www.jacplus.com.au.

1. What are the main energy transformations occurring in:
   (a) a galvanic cell? 
   (b) an electrolytic cell?
2. Explain why the cathode is positive in a galvanic cell but negative in an electrolytic cell.
3. Explain why the anode is negative in a galvanic cell but positive in an electrolytic cell.

studyON
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7.6 Calculations in electrolysis using Faraday’s Laws

KEY CONCEPT
- The application of stoichiometry and Faraday’s Laws to determine amounts of product, current or time for a particular electrolytic process
MICHAEL FARADAY

Michael Faraday (1791–1867) was a bookbinder 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 in London, which is dedicated to scientific education and research. After 10 years of hard work, Faraday 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, but he is most famous for his work on electricity. 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.

7.6.1 Faraday’s first law of electrolysis

Faraday’s first law of electrolysis describes the relationship between the mass of a substance deposited or liberated during electrolysis and the quantity of electric charge passed through the cell. That is, mass is proportional to charge.

Faraday’s first law of electrolysis:

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 \((6.24 \times 10^{18} \text{ electrons})\) of charge flows every second. For example, if a current of 3.00 amperes flows for 10.0 minutes, the quantity of electricity is \((3.00 \times 10.0 \times 60) = 1.80 \times 10^3\) 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. 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 7.3.

<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 graph of these results (see figure 7.18) yields a straight line passing through the origin. This shows 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.

The charge on one electron is $1.602 \times 10^{-19}$ C.

Therefore, one mole of electrons 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$^{-1}$.

**TIP:** The Faraday constant, $96 500$ C mol$^{-1}$ can be found in table 4 of the VCE Chemistry Data Book.

### SAMPLE PROBLEM 5

When a current of 3.2 A is passed through a solution for 10.0 minutes, 0.010 mol of gas B is evolved.

What amount of B will be evolved if a current of 2.0 A is used for 15 minutes?

**THINK**
1. Charge used is calculated from the formula $Q = It$. The formula can be found in Table 3 of the VCE Chemistry Data Book.

**TIP:** When using $Q = It$, remember that units must be considered. While $t$ should be in seconds because we are using a ratio to determine the amount of B evolved, as long as the same units for time are used, they do not need to be converted to seconds.

**WRITE**

\[
Q = 3.2 \times 10.0 \times 60
= 1920 \text{ C (original)}
\]

\[
Q = 2.0 \times 15 \times 60
= 1800 \text{ C (new)}
\]
2. Recall that amount evolved is proportional to charge flowing through the cell (Faraday’s first law). Give your answer to two significant figures.

Amount B = 0.010 × \[
\frac{1800}{1920}
\] = 0.0094 mol (2 sig.fig)

PRACTICE PROBLEM 5

When a current of 3.4 A is passed through a solution for 7.0 minutes, 0.015 mol of metal X is deposited.

What amount of X will be deposited if a current of 2.5 A is used for 20 minutes?

7.6.2 Faraday’s second law of electrolysis

Faraday’s second law of electrolysis describes the stoichiometric relationship between the moles of substance produced by electrolysis and the moles of electrons required.

Faraday’s second law of electrolysis: 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:

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

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 \(\text{Ag}^+ (aq)\) 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 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: \(\text{Na}^+ + \text{e}^- \rightarrow \text{Na}\)
1 faraday must be passed to liberate 1 mole of sodium atoms (23.0 g).

Copper: \(\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}\)
2 faradays must be passed to liberate 1 mole of copper atoms (63.5 g).

Magnesium: \(\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}\)
2 faradays must be passed to liberate 1 mole of magnesium atoms (24.3 g).

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

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

The number of moles of electrons, \(n(e^-)\) (the number of faradays), corresponding to a given charge (in coulombs) can be determined by the equation:

\[n(e^-) = \frac{Q}{F}\]

where:

- \(n\) is the number of moles of electrons
- \(Q\) is the electrical charge in coulombs (C)
- \(F\) is the Faraday constant, 96 500 C mol\(^{-1}\).
SAMPLE PROBLEM 6

When 7720 C is passed through a copper(II) sulfate solution, 0.040 mol of copper is produced. If the same amount of charge is passed through a solution containing Ag$^+$ ions, how many moles of Ag will be produced?

**THINK**
1. Write the equation for the electrode reaction for both Cu and Ag deposition.
2. The reaction in step 1 shows that 2\(\text{F}\) of charge is required to deposit 1 mol of Cu. The same 2\(\text{F}\) will deposit 2 mol of Ag because it only has a single charge on its ion. Hence, there is a 2:1 ratio when equal amounts of charge are used. Give your answer to two significant figures.

**WRITE**

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

\[
n(\text{Ag}) = 2 \times n(\text{Cu}) = 2 \times 0.040 = 0.080\text{ mol}
\]

PRACTICE PROBLEM 6

When 7720 C is passed through a copper(II) sulfate solution, 0.040 mol of copper is produced. If the same amount of charge is passed through a solution containing W$^{3+}$ ions, how many moles of W will be produced?

7.6.3 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 can be solved by using the formulas:

\[
Q = It \\
n(e^-) = \frac{Q}{F}
\]

where:
\(Q\) = the electrical charge (C)
\(I\) = the current (A)
\(t\) = the time (s)
\(F\) = 96,500 C mol\(^{-1}\).

Together these relationships summarise Faraday’s two laws of electrolysis.

SAMPLE PROBLEM 7

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.
THINK
a. 1. To determine the mass of copper deposited, first calculate the amount of charge and convert it to faradays (same as moles of charge). Remember to convert time to seconds.

\[ Q = It \]
\[ = 0.500 \times (30.0 \times 60) \]
\[ = 900 \text{ C} \]

2. Determine the equation at the cathode and the number of moles of electrons.

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu(s)} \]
\[ n(e^-) = \frac{Q}{F} \]
\[ = \frac{900}{96500} \]
\[ = 9.33 \times 10^{-3} \text{ mol} \]

3. Use stoichiometry involving electrons to calculate moles of copper produced. One mole of copper requires two moles of electrons.

\[ n(\text{Cu}) = \frac{n(e^-)}{2} \]
\[ = \frac{9.33 \times 10^{-3}}{2} \]
\[ = 4.67 \times 10^{-3} \text{ mol} \]

4. Determine the mass of the copper produced using the molar mass formula.

\[ m(\text{Cu}) = n \times M \]
\[ = (4.67 \times 10^{-3}) \times 63.5 \]
\[ = 0.296 \text{ g} \]

**TIP:** Formulas and the value of the Faraday constant can be found in Tables 3 and 4 of the VCE Chemistry Data Book.

b. 1. Determine the equation at the anode.

2. Using the number of electrons determined in step a. 1., use stoichiometry involving electrons to calculate moles of oxygen produced. There is one mole of oxygen to four moles of electrons.

3. Determine the volume of oxygen produced using the molar volume formula.

\[ n = \frac{V}{V_m} \]
\[ V(\text{O}_2)_{\text{SLC}} = n \times V_m \]
\[ = (2.33 \times 10^{-3}) \times 24.8 \]
\[ = 0.0578 \text{ L} \text{ or } 57.8 \text{ mL} \]

WRITE

\[ Q = It \]
\[ = 0.500 \times (30.0 \times 60) \]
\[ = 900 \text{ C} \]

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu(s)} \]
\[ n(e^-) = \frac{Q}{F} \]
\[ = \frac{900}{96500} \]
\[ = 9.33 \times 10^{-3} \text{ mol} \]

\[ n(\text{Cu}) = \frac{n(e^-)}{2} \]
\[ = \frac{9.33 \times 10^{-3}}{2} \]
\[ = 4.67 \times 10^{-3} \text{ mol} \]

\[ m(\text{Cu}) = n \times M \]
\[ = (4.67 \times 10^{-3}) \times 63.5 \]
\[ = 0.296 \text{ g} \]

PRACTICE PROBLEM 7

A solution of copper(II) sulfate is electrolysed for 17.5 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.

SAMPLE PROBLEM 8

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?

Teacher-led video: SP8 (tlvd-0700)
THINK
1. To determine the charge on the calcium ion, first determine the number of moles of calcium.

\[
n(Ca) = \frac{m}{M} = \frac{0.0401}{40.1} = 0.00100 \text{ mol}
\]

2. Determine the amount of electricity used and the number of moles of electrons. Compare the units given to those required. Time must be in seconds.

\[
Q = It = 0.200 \times 965 = 193 \text{ C}
\]

\[
n(e^-) = \frac{Q}{F} = \frac{193}{96500} = 0.00200 \text{ mol}
\]

3. According to step 2, 0.00200 moles of electrons are needed to produce 0.00100 moles of calcium. Let the charge on ions will be \( x^+ \). Use stoichiometry to calculate \( x \).

\[
\frac{n(e^-)}{x} = \frac{n(Ca)}{x} = \frac{0.00200}{0.00100} = 2
\]

The charge on the calcium ion is 2+ (Ca\(^{2+}\)).

PRACTICE PROBLEM 8
When a molten aluminium chloride solution is electrolysed by a current of 0.300 A flowing for 965 seconds, 0.0270 g of aluminium is formed. What is the charge on the aluminium ion?

Faraday’s Laws in industry
Calculations based on Faraday’s Laws are critical to industrial electrolytic processes. Due to the large scale of these processes, small variations and inefficiencies can 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 9
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.

Teacher-led video: SP9 (tlvd-0701)

THINK
1. Determine the equation at the cathode.

\[
\text{WRITE}
\]

\[
\text{Al}^{3+}(l) + 3e^- \rightarrow \text{Al}(l)
\]
2. Calculate the amount of charge used by applying the formula \( Q = It \).

   \[
   Q = 1.70 \times 10^4 \times (24 \times 60 \times 60)
   \]
   \[
   = 1.47 \times 10^9 \text{ C}
   \]

   \[
   n (\text{electrons}) = \frac{Q}{F}
   \]
   \[
   = \frac{1.47 \times 10^9}{96500}
   \]
   \[
   = 1.52 \times 10^4 \text{ mol}
   \]

3. Using the number of moles of electrons determined in step 2, use stoichiometry involving electrons to calculate the moles of aluminium produced. There is one mole of aluminium to three moles of electrons.

   \[
   n (Al) = \frac{1.52 \times 10^4}{3}
   \]
   \[
   = 5.07 \times 10^3 \text{ moles of Al}
   \]

4. Convert moles to mass of aluminium using the molar mass formula, \( n = \frac{m}{M} \).

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

**PRACTICE PROBLEM 9**

Calculate the mass of magnesium produced over 24 hours when a current of 10 000 A is used.

---

7.6 EXERCISES

To answer questions online and to receive immediate feedback and sample responses for every question go to your learnON title at www.jacplus.com.au.

1. When 2200 C is passed through a copper(II) sulfate solution, 0.011 mol of copper is produced. If the same amount of charge is passed through a solution containing Cr^{3+} ions, how many moles of Cr will be produced?

2. A solution of silver nitrate is electrolysed for 20.0 minutes using a current of 0.600 A. Calculate:
   (a) the mass of silver deposited at the cathode
   (b) the volume (at SLC) of oxygen gas evolved at the anode.

3. When a solution containing gold ions is electrolysed by a current of 0.100 A flowing for 965 seconds, 0.197 g of gold is formed. What is the charge on the gold ion?

4. How long will it take to deposit 1.00 g of cobalt in an electrolytic cell that uses a current of 3.50 A? The equation for the reduction is Co^{2+}(aq) + 2e^{-} \rightarrow Co(s).

5. A current of 4.25 A is passed through molten Al_2O_3 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 29.0 °C, would be evolved?

6. 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?

7. A given quantity of electricity is passed through two aqueous cells connected in series. The first contains silver chloride and the second contains calcium chloride. What mass of calcium is deposited in one cell if 2.00 g of silver is deposited in the other cell?
8. 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.

9. For the following scenarios:
   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 and 25 minutes
   iv. a current of 2.4 A flows for 1.0 day.
   Calculate:
   a) the mass of copper deposited during the electrolysis of aqueous copper(II) sulfate using carbon electrodes
   b) the volume of oxygen formed at SLC during the electrolysis of aqueous copper(II) sulfate using carbon electrodes.

10. 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.)

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7.7 Rechargeable batteries (secondary cells)

KEY CONCEPT
- The operation of rechargeable batteries (secondary cells) with reference to discharging as a galvanic cell and recharging as an electrolytic cell, including the redox principles (redox reactions and polarity of electrodes) and the factors affecting battery life with reference to components and temperature (no specific battery is required).

TIP: Some examples of secondary cells are provided in this subtopic. Although you are not required to know the details of any specific cell, you should examine these examples and make sure that you understand the principles behind their operation. It is expected that you should be able to apply these principles in an examination, rather than just restating facts that you have learnt.

7.7.1 What is a secondary cell?
A secondary cell is essentially a galvanic cell combined with an electrolytic cell.

Secondary cells, often referred to as rechargeable batteries, are devices that can be recharged when they become ‘flat’. They are 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 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, their ability to be recharged many hundreds of times makes them a cheaper alternative in the long-term.

**Lead–acid accumulator**

Developed in the late-nineteenth century, the lead–acid accumulator has remained the most common and durable of battery technologies. Lead–acid accumulators are secondary cells. They have a relatively long life 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 provides electricity for 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 (see figure 7.19).

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 (the negative terminal) of the cell is packed with spongy lead. The grid that form the cathode (the positive terminal), is packed with lead(IV) oxide, PbO$_2$. The electrodes are both immersed in approximately 4 M sulfuric acid and are separated by a porous plate.

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

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

At the anode, lead is oxidised to Pb$^{2+}$ ions. These react immediately with the sulfuric acid solution to produce insoluble lead(II) sulfate, which deposits on the grid.

At the cathode, lead(IV) oxide is reduced to Pb$^{2+}$ 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:

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

Note that the pH of the cell increases during the discharge cycle.
The recharging process in a lead–acid accumulator

The products of the discharge process remain as a deposit on the electrodes. This means that the reactions at these electrodes can 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.

While 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.

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

Note that the pH of the cell decreases during the recharge cycle.

This reaction is not spontaneous so 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.

In theory, a lead storage battery can be recharged indefinitely, but in practice it may only last for 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.
Nickel–metal hydride (NiMH) 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. An additional 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:

Oxidation takes place at the (anode):

\[
\text{Anode: } MH(s) + OH^-(aq) \rightarrow M(s) + H_2O(l) + e^- \quad \text{(note the } M \text{ here refers to a metal)}
\]

Reduction takes place at the positive electrode (cathode):

\[
\text{Cathode: } \text{NiO(OH)}(s) + H_2O(l) + e^- \rightarrow \text{Ni(OH)}_2(s) + OH^-(aq)
\]

Overall equation:

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

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

LITHIUM–ION BATTERIES

A new type of cell rapidly gaining popularity in portable devices such as digital cameras, phones and computers is the lithium–ion battery. These 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 over-discharged, they cannot be recharged. On the other hand, if they are over-charged, 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, but this adds to their cost.

FIGURE 7.21 A nickel–metal hydride cell for a digital camera

Key
- metal hydride anode
- nickel cathode
- separator
- top cover
- cathode lead
- safety insulator
- can

FIGURE 7.22 The Mars Exploration Rovers Spirit and Opportunity were powered by lithium–ion batteries, which are light and reliable.
7.7.2 Factors affecting battery life

While there are specialist batteries designed to operate at extreme temperatures, the 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 over-discharge 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. Unwanted side reactions are more likely to occur.

7.7 EXERCISES

To answer questions online and to receive immediate feedback and sample responses for every question go to your learnON title at www.jacplus.com.au.

1. During the recharging process for the lead–acid accumulator, will the pH of the contents rise or fall? Explain.
2. Explain why the positive terminal of the charging device must be connected to the positive terminal of the battery, and the negative to the negative, when a rechargeable battery is to be recharged.
3. The nickel-cadmium rechargeable cell was a widely-used predecessor to today's nickel–metal hydride cells and lithium–ion cells. The figure shows some of the components of this type of cell.

![Diagram of nickel-cadmium cell]

The cell contains cadmium and NiO(OH) as its reactants. These are kept apart by a porous separator that has been soaked in KOH. During discharge, the reaction at the anode is:

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

The overall cell reaction is:

\[
\text{Cd(s)} + 2\text{NiO(OH)}(\text{s}) + 2\text{H}_2\text{O(l)} \rightarrow \text{Cd(OH)}_2(\text{s}) + 2\text{Ni(OH)}_2(\text{s})
\]
(a) Write the equation that occurs at the cathode during recharging.
(b) During recharging, what terminal of the recharging device should the anode be connected to?
(c) Write the equation for the overall cell reaction during the recharging process.
(d) Write the equation for the reaction that occurs at the anode during recharging.

4. Batteries based on vanadium chemistry are increasingly being used to store energy from solar panels. During the day, solar cells store energy in the battery as it is charged. At night, the battery functions as a galvanic cell, producing electricity to power the household.

The two relevant half-equations for the functioning of this battery are:

\[
\begin{align*}
\text{VO}^2+(aq) + 2H^+(aq) + e^- &\rightarrow \text{VO}^{2+}(aq) + H_2O(l) \quad E^0 = +1.00 \text{ V} \\
\text{V}^3+(aq) + e^- &\rightarrow \text{V}^{2+}(aq) \quad E^0 = -0.26 \text{ V}
\end{align*}
\]

(a) Write the overall equation for this battery as it is discharging.
(b) Write the overall equation for this battery as it is recharging.
(c) Write the half-equations for the reactions occurring at each electrode as the cell recharges.

5. 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:

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

(a) Give electrode reactions during:
   i. discharging
   ii. recharging.
(b) What materials would be used for the electrodes?
(c) In the discharge process, which electrode is the anode and which is the cathode?
(d) In the recharge process, which electrode is the anode and which is the cathode?

---

**7.8 Review**

### 7.8.1 Summary

**What is electrolysis?**

- 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.
- The electrolysis of a single molten salt forms products that are easily predicted.
- The electrolysis of water to which a tiny amount of electrolyte has been added forms hydrogen gas and oxygen gas.

**Predicting reactions that occur during electrolysis**

- 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.
- The electrochemical series can be used to predict reactions where more than one species is available for reaction at an electrode.
- Cations of reactive metals, including aluminium, cannot be reduced from aqueous solutions because water is a stronger oxidising agent and is preferentially reduced.
Commercial applications of electrolysis

- 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, because production by chemical reduction is not practical.
- Chlorine, sodium hydroxide and hydrogen gas can be produced industrially in the membrane cell according to the overall reaction:

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

- Aluminium can be produced industrially by the Hall–Héroult process according to the overall equation:

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

- 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.

Comparing galvanic and electrolytic cells

- Electrolytic cells differ from galvanic cells in a number of ways, which are summarised in the following table.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Galvanic cell</th>
<th>Electrolytic cell</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>

Calculations in electrolysis using Faraday’s Laws

- Faraday’s Laws can be applied to a range of problems involving quantitative calculations in electrolysis.
- Faraday’s first law of electrolysis can be summarised as:

\[ Q = It, \]

where:
\( Q \) is the electric charge in coulombs
\( I \) is the current in amperes
\( t \) is the time in seconds.
Faraday’s second law of electrolysis can be summarised as:

\[
\text{number of moles of electrons, } n(e^-) = \frac{Q}{F}
\]

where \( F \) is the Faraday constant representing the quantity of charge carried by 1 mole of electrons (96 500 coulombs).

**Rechargeable batteries (secondary cells)**

- 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:

\[
PbO_2(s) + 4H^+(aq) + Pb(s) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)
\]

The recharging process is the reverse of the discharging process and requires approximately 14 volts of DC power to occur according to the reaction:

\[
2PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + 4H^+(aq) + Pb(s) + 2SO_4^{2-}(aq)
\]

- The nickel–metal hydride cell takes advantage of the property that some metal alloys have of storing hydrogen atoms. The overall equation representing discharge is:

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

- 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.
- Physical factors that affect the integrity of a battery’s construction will also affect its life.

### 7.8.2 Key terms

- **anode**: the electrode at which oxidation occurs. In a galvanic cell, it is the negative electrode, because it is the source of negative electrons for the circuit. If the reducing agent is a metal, it is used as the electrode material.
- **cathode**: the electrode at which reduction occurs. In a galvanic cell, it is the positive electrode, because the negative electrons are drawn towards it and then consumed by the oxidising agent, which is present in the electrolyte.
- **electrochemical series**: a series of chemical elements arranged in order of their standard electrode potentials.
- **electrolysis**: the decomposition of a chemical substance (in solution or the molten state) by the application of electrical energy.
- **electrolytes**: liquids that can conduct electricity.
- **electrolytic cell**: an electric cell in which a non-spontaneous redox reaction is made to occur by the application of an external potential difference across the electrodes.
- **electroplating**: adding a thin metal coating by electrolysis.
- **Faraday constant**: a constant that represents the amount of electric charge carried by 1 mole of electrons.
- **Faraday’s first law of electrolysis**: The amount of current passed through an electrode is directly proportional to the amount of material released from it.
- **Faraday’s second law of electrolysis**: When the same quantity of electricity is passed through several electrolytes, the mass of the substances deposited are proportional to their respective chemical equivalent or equivalent weight.
- **Hall–Héroult**: the method of aluminium production used in primary aluminium smelters throughout the world.
- **lead–acid accumulator**: a battery with lead electrodes using dilute sulfuric acid as the electrolyte; each cell generates about 2 volts.
membrane cell: used for the electrolysis of brine
rechargeable: describes a battery that is an energy storage device; it can be charged again after being discharged by applying DC current to its terminals
recharging: forcing electrons to travel in the reverse direction and, because the discharge products are still in contact with the electrodes, the original reactions are reversed
secondary cell: a cell that can be recharged once its production of electric current drops; often called a rechargeable battery

7.8.3 Practical work and experiments

Experiment 7.1
Electrolysis of aqueous solutions
Aim: To conduct electrolysis on aqueous solutions and test for the products at each electrode
Digital document: doc-31264
Teacher-led video: tlvd-0749

Experiment 7.3
Electroplating
Aim: To plate a piece of copper with nickel metal.
Digital document: doc-31266
Teacher-led video: tlvd-0751

7.8 Exercises

To answer questions online and to receive immediate feedback and sample responses for every question go to your learnON title at www.jacplus.com.au.

7.8 Exercise 1: Multiple choice questions

1. In an electrolytic cell:
   A. the cathode is positive and it is the site of reduction
   B. the cathode is negative and it is the site of oxidation
   C. the anode is positive and it is the site of reduction
   D. the cathode receives electrons from the external power source.
2. During the operation of an electrolytic cell:
   A. there is a flow of electrons through the solution between the cathode and anode
   B. inert electrodes must always be used
   C. a salt bridge is required to complete the circuit
   D. electrical energy is converted into chemical energy.
3. Which 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.
4. Which 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. 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.
6. 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.
7. Consider the following standard reduction potentials.
   \[
   \begin{align*}
   \text{Zn}^{2+} (aq) + 2e^- & \rightleftharpoons \text{Zn(s)} & \quad E^0 &= -0.76 \text{V} \\
   2\text{H}^+ (aq) + 2e^- & \rightleftharpoons \text{H}_2(g) & \quad E^0 &= 0.00 \text{V} \\
   \text{Ag}^+ (aq) + e^- & \rightleftharpoons \text{Ag(s)} & \quad E^0 &= +0.80 \text{V} \\
   2\text{H}_2\text{O(l)} + 2e^- & \rightleftharpoons \text{H}_2(g) + 2\text{OH}^- (aq) & \quad E^0 &= -0.83 \text{V}
   \end{align*}
   \]
   Which product would be liberated first at the cathode if a solution containing \(\text{Zn(NO}_3)_2\) and \(\text{AgNO}_3\) is electrolysed with platinum electrodes?
   A. \(\text{H}_2(g)\)
   B. \(\text{Ag(s)}\)
   C. \(\text{Zn(s)}\)
   D. \(\text{OH}^- (aq)\)
8. Which of the following groups of substances would normally be extracted by electrolysis in a non-aqueous environment?
   A. Iron, nickel and chromium
   B. Gold, copper, silver and platinum
   C. Magnesium, aluminium, sodium and chlorine
   D. Oxygen, neon, argon and nitrogen.
9. 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).

10. A solution contains CuCl\(_2\), NiCl\(_2\) and ZnCl\(_2\), with 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. Cu\(^{2+}\)(aq) + 2e\(^-\) → Cu(s)
   B. Ni\(^{2+}\)(aq) + 2e\(^-\) → Ni(s)
   C. Zn\(^{2+}\)(aq) + 2e\(^-\) → Zn(s)
   D. 2Cl\(^-\)(aq) → Cl\(_2\)(g) + 2e\(^-\)

11. 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.

12. In a rechargeable battery:
   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.

13. During the discharging process in a lead–acid accumulator:
   A. the concentration of hydrogen ions, H\(^+\), increases, resulting in an increase in pH
   B. the concentration of hydrogen ions, H\(^+\), decreases, resulting in a decrease in pH
   C. the concentration of hydrogen ions, H\(^+\), increases, resulting in a decrease in pH
   D. the concentration of hydrogen ions, H\(^+\), decreases, resulting in an increase in pH.

14. The cathode reaction during discharge in a nickel–metal hydride cell is:

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

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 reaction occurs at the negative electrode.
   D. Oxidation occurs at the surface of the negative electrode.

15. 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 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.
7.8 Exercise 2: Short answer questions

1. 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>Electrodes</th>
<th>Anode (+)</th>
<th>Cathode (−)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molten salt</td>
<td>Inert</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 M aqueous salt solution</td>
<td>Inert</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 M aqueous salt solution</td>
<td>Inert</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. 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.

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

4. For each of the following, predict the products at the anode and cathode, determine the minimum cell voltage required for the electrolysis (using carbon electrodes) of 1.0 M aqueous solutions and write an overall equation.
   a. potassium hydroxide
   b. potassium sulfate
   c. magnesium chloride
   d. zinc bromide
   e. sodium iodide
   f. hydrochloric acid
   g. sulfuric acid

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

6. In what ways are galvanic and electrolytic cells:
   a. similar?
   b. different?

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

8. Which of the following temperature ranges would be expected to result in the greatest number of recharge cycles for most rechargeable batteries? Explain.
   a. 30 °C to 45 °C
   b. 25 °C to 35 °C
   c. 5 °C to 25 °C
   d. −10 °C to 10 °C
9. 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 electrode.

10. 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?

11. 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 electrons are transferred?
   c. How many moles of chromium are liberated?
   d. What is the charge on the chromium ion?

12. a. What volumes of hydrogen gas, H₂, and oxygen gas, O₂, 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 question 12a.

13. Sir Humphry Davy discovered sodium by electrolysing molten sodium hydroxide. How long must a current of 1.5 A flow to produce 1 g of sodium? Give your answer in minutes.

14. A given quantity of electricity is passed through three cells connected in series. These cells contain solutions of silver nitrate, tin (II) chloride and magnesium chloride respectively, all at 1 M concentration. All cells have inert electrodes. After a period of time it is observed that 2 g of silver has been deposited in the first cell.
   a. What mass of tin would have been deposited in the second cell?
   b. What mass of magnesium would have been deposited in the third cell?

15. 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 cm². 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.

7.8 Exercise 3: Exam practice questions

Question 1  (9 marks)
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.
   b. Write half-equations for the expected reactions at each electrode, and then write the overall equation.
   c. Calculate the minimum voltage needed to electrolyse the solution under standard conditions (SLC).
   d. Explain how the products of electrolysis would differ if nickel electrodes were used.
**Question 2** (6 marks)

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 calculate the number of moles of electrons consumed. 2 marks

d. Calculate the charge on 1 mole of electrons. 1 mark

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

**Question 3** (5 marks)

What mass (in kg) of chlorine gas is produced in 1 hour 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

**Question 4** (12 marks)

Sodium is made commercially by the electrolysis of molten sodium chloride in a Downs cell. This cell contains an iron cathode and a carbon anode, and design features to collect and keep the products of electrolysis separate. A number of methods can be used to reduce the melting temperature of the sodium chloride and save on energy costs. A common method is to add an amount of calcium chloride to the melt.

The following diagram shows the essential features of this cell.

---

**Diagram:**

- Cathode: Na (liquid)
- Anode: Carbon electrode
- Molten NaCl
- Perforated iron plate
- Cl₂(g)
- Recharge of NaCl

---

a. Which electrode forms the positive electrode and which electrode forms the negative electrode? 1 mark

b. Write the equation for the half-reaction occurring at the anode. 1 mark

c. Write the equation for the half reaction occurring at the cathode. 1 mark

d. Suggest why the perforated iron plate, shown in the diagram, is important for the safe operation of this cell. 1 mark

e. Explain why the carbon electrode cannot be replaced with an iron electrode. 3 marks

f. Explain why the addition of calcium chloride does not interfere with the production of sodium. 2 marks

g. Calculate the volume of Cl₂ gas, measured at SLC, that would be produced when this cell operates with a current of 2.50 A for 12.00 hours. 3 marks
Question 5 (10 marks)
Both silver and gold may be electroplated onto an object to make it more attractive or resistant to corrosion. The electroplating of silver uses a silver anode and an aqueous solution that contains silver cyanide \((\text{AgCN})\). The electroplating of gold uses an inert electrode and an aqueous solution containing potassium gold (I) cyanide \((\text{KAu(CN}_2)\)).

a. To which electrode does the object to be electroplated need to be attached?  
1 mark

b. Write the equation for the reaction occurring at the cathode
   i. during silver plating
   ii. during gold plating
2 marks

c. Write the equation for the reaction occurring at the anode
   i. during silver plating
   ii. during gold plating
2 marks

d. Explain why a silver anode can be used for silver plating but a gold anode cannot be used for gold plating.  
1 mark

e. The concentration of the relevant ion in the electrolyte is one of the factors that determines the quality of the coating. Why does this have to be monitored more closely in gold plating than in silver plating?  
1 mark

f. Calculate the mass of gold deposited when a current of 3.00 A flows for 100 seconds.  
3 marks